

Development and Applications of the Rapid Analysis of Post-Irradiation Debris (RAPID) Method to Nuclear Materials

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Emilie Fenske

May 2020

Copyright © 2020 by Emilie Kiersten Fenske

All rights reserved.

ACKNOWLEDGEMENTS

I would first like to thank my mentors at Oak Ridge National Laboratory, Dr. Ben Roach and Dr. Cole Hexel, who helped guide me through my research, as well as Joe Giaquinto for his willingness to support my PhD in his group and Dr. Vince Jodoin for his mentorship and advice. Their experience and guidance have been of great assistance, and I would not be where I am today without them. I would further like to thank my UTK advisor and committee members, Dr. Howard Hall, Dr. Steve Skutnik, Dr. Alan Icenhour, and Dr. Robert (Pete) Counce, for their enthusiasm in the classroom and time spent helping me to further develop and enhance this research.

I would also like to thank the staff members of NACIL in 4501; without their areas of expertise, and willingness to teach a nuclear engineer analytical chemistry, this research would have taken much longer to complete. Additionally, I would like to thank Dan Archer and Michael Willis for their assistance as my local ORNL radiation detection experts who never tired of me asking questions and using their espresso machine.

Lastly, my gratitude would not be complete without the acknowledgement of my friends and family who formed my support network throughout this period. I would particularly like to thank my mom and dad for their unending support and love. I would also like to thank Ian Stewart, Alex Braatz, Adam Stratz, Jon Gill, Matthew Duchene, Josh Chandler, Lloyd Ramey, and David Glasgow for their ever-present encouragement and motivation.

PREFACE

This dissertation is an original intellectual product of the author, Emilie K. Fenske, and was performed under contract No. DE AC05-00OR22725. This work was sponsored by the Defense Threat Reduction Agency (DTRA). This research was supported in part by an appointment to the Oak Ridge National Laboratory Post-Master's Research Associate Program, sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education. The views and conclusions contained in this document are those of the author and should not be interpreted as representing the official policies, either expressed or implied, of the supporting entities.

Portions of the text, as specified within the chapters, elaborate on scientific articles of which I am an author.

All of the work presented henceforth was conducted at Oak Ridge National Laboratory.

ABSTRACT

Chemical analysis of nuclear materials is a well-developed area of research, through use of mass spectrometers and other destructive analysis techniques. These analyses are applicable to several nuclear fields, such as nuclear forensics, fuel characterization and modeling, and environmental monitoring. For nuclear forensics particularly, a rapid analytical chemistry technique can be useful, given the need for a quick turn-around of data in certain attribution cases for nuclear forensics.

An analytical technique for low-level nuclear material analyses has been developed and applied to various samples at Oak Ridge National Laboratory (ORNL), named Rapid Analysis of Post-Irradiation Debris (RAPID). This technique combines a high-pressure ion chromatography unit and an inductively-coupled plasma mass spectrometer for a rapid, direct separation-detection method, with a turn-around of less than four hours per sample, including dissolution, analysis, and data processing. Analyzed samples include irradiated highly-enriched uranium, ORNL-developed, and UTK-developed surrogate nuclear “debris”. This dissertation will present the development of RAPID and its subsequent evolution and application to nuclear forensics, obtaining the sensitivity and accuracy for operational usage at ORNL.

Additionally, a novel inline gamma detection technique was developed as an extension of RAPID and will be presented, demonstrating the feasibility of elementally-isolated gamma spectrometry and the benefit of having two complementary analytical techniques to fully characterize fission products in a short timeframe.

Table of Contents

ACKNOWLEDGEMENTS	iii
PREFACE.....	iv
ABSTRACT.....	v
CHAPTER 1: INTRODUCTION.....	1
<i>1.1 Background: Post-detonation Nuclear Forensics</i>	<i>1</i>
<i>1.2 Current Analytical Challenges</i>	<i>2</i>
<i>1.3 The Rapid Analysis of Post-Irradiation Debris Protocol</i>	<i>4</i>
<i>1.4 Post-Detonation Debris Samples.....</i>	<i>5</i>
1.4.1 ORNL Debris Generation.....	5
1.4.2 UTK Surrogate Debris Generation.....	6
<i>1.5 Dissertation Objective</i>	<i>7</i>
CHAPTER 2: LITERATURE SURVEY	8
<i>2.1 Focus of this Review</i>	<i>8</i>
2.1.1 Materials of Interest	9
2.1.2 Overview of the Sample Analysis Process.....	11
2.1.3 Rapid Analytical Techniques for Post-Detonation Nuclear Forensics.....	13
<i>2.2 Overview of Mass Spectrometry Techniques.....</i>	<i>15</i>
2.2.1 Inductively-Coupled Plasma Mass Spectrometry	15
2.2.2 Secondary Ionization Mass Spectrometry (SIMS).....	17
2.2.3 Thermal Ionization Mass Spectrometry (TIMS).....	18

2.3 Chemical Separation Techniques	18
2.3.1 Chemical Separations Overview	18
2.3.2 Ion Chromatography (IC).....	20
2.4 Inline Radiation Detectors.....	23
CHAPTER 3: THEORY	25
3.1 Scope.....	25
3.2 Overview of Basic Chemistry Principles	25
3.2.1 Lanthanide Properties.....	25
3.2.2 Uranium Solution Properties	26
3.2.3 Separation Chemistry	26
3.2.4 Quadrupole ICPMS	30
3.2.5 ICPMS Instrumental Mass Bias	41
3.2.6 Isotope Dilution Mass Spectrometry	44
3.3 Radiation Detection Principles.....	53
3.3.1 Solid Angle Concept	56
3.4 Uncertainty Calculations.....	57
CHAPTER 4: EXPERIMENTAL	58
4.1 Instrumentation and NACIL Capabilities.....	58
4.2 Nuclear Physics Modeling Codes.....	63
4.2.1 Fission Product Modeling	63
4.2.2 MCNP Detector Response Modeling	65

4.3 <i>Experimental Preparation</i>	67
4.3.1 <i>Eluent Preparation</i>	67
4.3.2 <i>HPIC-ICPMS Preparation</i>	70
4.3.3 <i>Microwave Dissolution Procedure</i>	71
4.3.4 <i>Sample Descriptions</i>	73
CHAPTER 5: RAPID METHOD DEVELOPMENT	75
5.1 <i>The RAPID Timeline</i>	75
5.2 <i>Previous Work</i>	75
5.3 <i>Separations in a Soil Matrix</i>	80
5.3.1 <i>Journal of Chromatography A Publication</i>	80
5.3.2 <i>Methodology</i>	81
5.3.3 <i>Results and Discussion</i>	85
5.4 <i>Separations in a Surrogate Debris Matrix</i>	94
5.4.1 <i>Methodology</i>	94
5.4.2 <i>Results and Discussion</i>	97
CHAPTER 6: IRRADIATED FISSION PRODUCT ANALYSIS WITH RAPID	103
6.1 <i>JRNC Publication</i>	103
6.2 <i>Talanta Publication</i>	104
6.3 <i>Methodology</i>	105
6.3.1 <i>Nuclear Material Characterization and Sample Preparation</i>	105
6.3.2 <i>ORIGEN Modeling</i>	106

6.3.3 HEU Post-Irradiation and RAPID Analysis	108
6.4 Results and Discussion	111
6.4.1 Material Analyses.....	111
6.4.2 Analysis of Targets 1 & 2	114
6.4.3 Analysis of Target 3	122
6.5 RAPID's Nuclear Forensics Analytical Gap.....	131
CHAPTER 7: DEVELOPMENT OF AN INLINE CZT DETECTION SYSTEM	135
7.1 JRNC Publication.....	135
7.2 Method Development.....	137
7.3 Results and Discussion	141
7.3.1 MCNP Simulated Spectra	141
7.3.2 Long Dwell Time CZT Measurements Post-Separation	147
7.3.3 Transient CZT Gamma Chromatograms.....	156
7.3.4 Fraction Collection HPGe Measurements.....	164
CHAPTER 8: CONCLUSION.....	171
8.1 Research Highlights and Conclusions.....	171
8.2 Publication Highlights.....	172
8.3 Lessons Learned – Applied Scenario.....	174
8.4 Areas of Continuation.....	176
CHAPTER 9: FUTURE WORK	177
REFERENCES.....	188

APPENDIX.....	214
VITA	220

LIST OF TABLES

Table 1. Summary of the destructive analytical techniques used in the 2016 nuclear forensics exercise ² .	3
Table 2. Laboratory Methods and Techniques with Typical Completion Timescales ³⁶	14
Table 3. Examples of ICPMS Interferences ⁵⁴	17
Table 4. Eichrom Resins and Selectivity ¹⁰⁷	20
Table 5. Comparison of material/detector characteristics between HPGe and CZT ^{192,193}	55
Table 6. CZT operating parameters within the Canberra Lynx system.	61
Table 7. Eluent properties	69
Table 8. ICPMS and HPIC operating parameters.	71
Table 9. Microwave dissolution parameters	72
Table 10. Modified separation scheme elution profile.	78
Table 11. Recoveries of the spiked lanthanides in IV-ICPMS-071A calculated with IDMS ²⁰⁹ .	78
Table 12. Surrogate soil composition, showing compounds used and elemental weight fractions ²⁰⁹ .	83
Table 13. Element concentrations for the IDMS analysis with the surrogate soil matrix.	84
Table 14. Concentrations of the NIST 2711a soil and IDMS spike pre-dissolution.	84
Table 15. Stability and retention times in the surrogate soil matrix ¹⁹⁸ .	89
Table 16. Isotopic LOD/LOQs with and without the surrogate soil matrix ¹⁹⁸	92
Table 17. Final recoveries of the spiked elements within the surrogate soil matrix.	94
Table 18. RAPID IDMS values compared to NIST certified values of SRM 2711a soil.	94
Table 19. Detection limit study results in a contaminated ORNL surrogate debris matrix.	99

Table 20. Original debris composition compared to the measured composition post-dissolution with offline ICPMS analysis.	102
Table 21. IDMS recoveries of selected lanthanides in both UTK surrogate debris matrices. ...	102
Table 22. Irradiation and decay details for each HEU target.	107
Table 23. Irradiation parameters used for ORIGEN models.	108
Table 24. Target 3 timeline from irradiation to analyses with both HPGe and RAPID.	111
Table 25. HEU standard U930-D lanthanide concentrations pre-irradiation.	113
Table 26. Measured cesium isotopic abundances for both targets compared with the predicted ORIGEN ratio at 36.1 days decay post-irradiation ²⁰⁸	117
Table 27. Measured vs. ORIGEN-predicted cerium ratios in both targets using a 36.1 day decay time ²⁰⁸	118
Table 28. Measured neodymium atom percent abundances of each isotope as compared to naturally-occurring and ORIGEN-generated fission-induced abundances. The average, corrected fission abundances of the targets is calculated ²⁰⁸	119
Table 29. Summary of the isotopic ratio recoveries compared to ORIGEN for Targets 1 and 2 ²⁰⁸	121
Table 30. RAPID-generated results from 10/2/2019 comparing calculated mass measured to ORIGEN-predicted mass.	123
Table 31. HPGe measurement from 10/03/2018 compared with ORIGEN data.	124
Table 32. Secondary leach measurement performed by offline ICPMS on 10/24/2018.	125
Table 33. 10/2/2018 cesium isotopic data compared to ORIGEN, assuming xenon loss at 24 h post-irradiation.	126

Table 34. Measured atom % by RAPID compared to those calculated in ORIGEN over six weeks post-irradiation. ORIGEN cesium numbers, highlighted in red, are updated from the published paper ²¹²	128
Table 35. Measured vs. ORIGEN-predicted atom percent ratios for neodymium at the three different analysis times post-irradiation, with three ratios shifting either up or down due to radioactive decay ²¹²	130
Table 36. HEU fission product isotopes quantified with each analytical technique. *isotopes quantified with both techniques.....	134
Table 37. Gamma-emitting isotopes in the fuel sample (bolded isotopes are within CZT calibration and readily separated)	138
Table 38. HPGe measurements of the AW from the TAL, performed on 7/25/2019. Highlighted in red are isotopes that should be identifiable by CZT and separated with RAPID.	140
Table 39. Approximate injected activities for each isotope per CZT analysis (performed on 10/8/2019) in both curies and becquerels.	141
Table 40. Source definitions used in MCNP input files, shown as gamma energies and relative intensities.	142
Table 41. Gammas and x-rays characteristic of the radioactive isotopes in the AW sample. ...	161
Table 42. List of all gammas identified in the ruthenium HPGe spectrum post-separation.	165
Table 43. List of all gammas identified in the europium HPGe spectrum post-separation.	170
Table 44. List of elements and the correlating standard used for each.	215

LIST OF FIGURES

Figure 1. The reporting time horizon for analytical techniques for the 2016 exercise as illustrated by Schwantes ² et al.	3
Figure 2. A light microscope image of larger, 1 mm glassy particles (right), and a focused ion beam was used to visualize the inside of a melted surrogate debris particle (left) by the PER group.	6
Figure 3. Samples of UTK surrogate debris, produced by Giminaro ¹¹ et al.....	6
Figure 4. Fission product spectrum as a function of mass number ³³	10
Figure 5. Fission-generated elements (highlighted in orange) and the lanthanides (noted in black square).....	10
Figure 6. A summary of analytical sequences and methods typically used in the context of nuclear forensics investigations as illustrated by Croudace ³⁵ et al.....	14
Figure 7. An HPLC Schematic Diagram ¹¹⁴	21
Figure 8. Examples of offline ¹²⁷ (left) vs. online ¹⁵⁷ IC-ICPMS (right) schematics.....	23
Figure 9. Potential chemical interactions at each stage for each ion going through the RAPID process.....	29
Figure 10. Dionex separation of transition metals and lanthanides in a single injection by IC ¹⁷⁸	29
Figure 11. Schematic diagram of the major components of an ICPMS quadrupole instrument as illustrated by Linge ¹⁷⁹ et. al.	31
Figure 12. A schematic diagram of a quadrupole mass filter, as illustrated by Linge ¹⁷⁹ et al. Voltages are applied to the rods (positive and negative as shown) in such a way that only ions with a single m/z have a stable path and exit the quadrupole.	34

Figure 13. Thermo iCAP-Q instrumental schematic ¹⁸¹	36
Figure 14. Right: the nebulizer (1), spray chamber (2), injector (3), and torch (4). Left: the torch and injector separately ¹⁸¹	36
Figure 15. Right: the interface block (1) and the plasma door (2). Left: a view of the extraction lens, located behind the cones (side not shown on the right) ¹⁸¹	38
Figure 16. Effect of dwell time on a neodymium peak using the RAPID protocol.	40
Figure 17. ICPMS interface diagram ¹⁸⁷	42
Figure 18. An example of the mass bias trend in a neodymium standard, measured with the RAPID system, where Δm is the difference in mass from 144 as a ratio (142/144 to 150/144).	43
Figure 19. Illustration of the isotope dilution principle for an element containing two different isotopes, a and b ¹⁹¹	44
Figure 20. A calculated error magnification curve for an R_S of 25 and R_{sp} of 0.01, showing an optimal R_m at 0.05.	51
Figure 21. Simulated pulse height spectrum for a CZT detector from incident radiation with an energy of 300 keV by Toney ¹⁹⁶ et al.	55
Figure 22. Illustration of the source-detector relationship for a solid angle calculation.	56
Figure 23. Photos of the original coupled HPIC-ICPMS system in a radiological fume hood. ..	60
Figure 24. Updated HPIC-ICPMS system (2019), including a CZT detector and fraction collector.	60
Figure 25. A 3D-printed shield designed with CZT dimensions for use in fume hood (CZT and sample loop also pictured).	61

Figure 26. Process diagram of RAPID, where orange indicates a new addition to the original method. The sample line can be diverted inline to either of the orange additions 15 and 16 (or bypass both of them).....	62
Figure 27. Flow of data for the ORIGEN models, as illustrated by J. Knowles ²⁰¹ . The red square highlights the user inputs for this project, and the red circle shows the subsequent data output by the model.....	65
Figure 28. A side view of the CZT crystal (pink) within its aluminum housing (blue), surrounded by the cylindrical loop source (yellow).	66
Figure 29. A top view of the CZT crystal (pink) within its aluminum housing (blue), surrounded by the cylindrical loop source (yellow).	66
Figure 30. Ampoule filled via syringe (left), solution dried by heat lamp and air flow (middle), final sealed targets of certified reference standard U930-D (93.2% ²³⁵ U) in high-purity silica ampoules ²⁰⁸ . Inset: scale in mm (right).....	74
Figure 31. Separation scheme using deionized water (yellow/A), 6 mM PDCA (green/B), 100 mM DGA (blue/C), and 100 mM oxalic acid (pink/D) ⁸	77
Figure 32. Resulting chromatogram of 26 elements after separation ⁸	77
Figure 33. Modified separation scheme using deionized water (A), PDCA (B), DGA (C), and oxalic acid (D).....	78
Figure 34. Resulting chromatograms of the natural neodymium standard (left) and the spiked neodymium standard (right) after separation ²⁰⁹ . Highlighted in red is the ¹⁴² Nd trace.	79
Figure 35. Graphical representation of the elements that have been successfully separated from isobaric interferences versus the elements expected in post-detonation debris or acids used for preparation of the material ²⁰⁹	83

Figure 36. Chromatogram displaying 30 of the 48 elements monitored in a separation of a 100 ppb mix of standards in the surrogate soil matrix ²⁰⁹	87
Figure 37. Partial chromatogram of Figure 28, illustrating separation of cesium and strontium from their isobaric interferences ²⁰⁹	87
Figure 38. Partial chromatogram of Figure 28, demonstrating separation of iron from other first-row transition metals copper, nickel, and cobalt ²⁰⁹	88
Figure 39. Partial chromatogram of Figure 28 showing clear separation of the lanthanides, unaffected by the addition of a soil matrix ²⁰⁹	88
Figure 40. Elution profile overlaid with silicon and calcium chromatograms (normalized) from the surrogate soil and eluents, shown by the chromatograms following the shapes of the elution profiles.	90
Figure 41. August 2018 round robin timeline for ORNL.	95
Figure 42. Limits of detection for the lanthanides from three different detection limit studies performed with RAPID with three different matrices (nitric acid, clean surrogate soil, and complex ORNL surrogate debris).....	100
Figure 43. An ORIGEN-generated plot of fission product masses over the course of a 36-day decay after the irradiation of 80 µg ²³⁵ U for 48.5 minutes ²⁰⁹	107
Figure 44. Top: major sample process steps; middle: correlating photos to the process (ampoule, irradiation station, glass in leach); bottom: mini-vice used to crush ampoule.....	109
Figure 45. Varying retention times of the lanthanides in four different concentrations of nitric acid.....	113

Figure 46. ORIGEN-calculated fission product distributions for Target 1 (green circles) and Target 2 (purple squares) after an irradiation time of 48.5 minutes, where all isobars were summed ²⁰⁸ .	115
Figure 47. A 3-D chromatogram of m/z ranging from 141-156 illustrating separation between lanthanides. Inset: a 2D cut of the chromatogram with labels and elution times of all pertinent lanthanides ²⁰⁸ .	117
Figure 48. Chromatogram of the 147 m/z trace for Target 2 illustrating separation between neodymium, promethium, and samarium.	121
Figure 49. Elemental separation of the lanthanides, m/z 139–154, with elution time ranging from 1200–1800 s ²¹² .	126
Figure 50. RAPID measurements of m/z 147 as a function of time post-irradiation.	129
Figure 51. The resulting fission product “double hump curve” as produced by an offline ICPMS mass spectrum scan with offline and online measurements (and ORIGEN predictions) overlaid ²¹² .	131
Figure 52. The HPGe measurement of irradiated HEU in October 2018. Inset: the lack of a 662 keV gamma from ¹³⁷ Cs.	133
Figure 53. The HPGe measurement of irradiated HEU in November 2018. Inset: the existence of a ¹³⁷ Cs gamma.	133
Figure 54. RAPID data for the fuel sample with the selected elements labeled.	138
Figure 55. MCNP-generated ¹³³ Ba + ¹³⁷ Cs point source spectrum.	143
Figure 56. MCNP-generated ¹⁰³ Ru + ¹³⁴ Cs spectrum, showing both spectra overlaid at their relative intensities to each based off of Bq in the injected sample.	144

Figure 57. MCNP-generated $^{141}\text{Ce} + ^{144}\text{Ce}$ spectrum, showing both spectra overlaid at their relative intensities to each based off of Bq in the injected sample.	145
Figure 58. MCNP-generated $^{154}\text{Eu} + ^{155}\text{Eu}$ spectrum, showing both spectra overlaid at their relative intensities to each based off of Bq in the injected sample.	146
Figure 59. A magnified view of the MCNP-generated europium spectra in Figure 58.....	147
Figure 60. Spectrum of $^{133}\text{Ba} + ^{137}\text{Cs}$ button sources for calibration purposes.	148
Figure 61. Smoothed CZT gamma spectra of the unseparated fuel sample in two configurations: vial and loop. The loop configuration is a 20x of the vial concentration (calculated spectrum shown in purple for comparison).....	149
Figure 62. Transient gamma chromatogram of the used fuel sample. Due to the low sample activity, nothing above background can be seen with the sample loop's intrinsic 30 s dwell time.	151
Figure 63. Chemically-separated CZT spectra of cesium (raw data and smoothed data), cerium, and europium in the fuel sample with a dwell time of five minutes.	152
Figure 64. Left: decay scheme of ^{137}Cs . Right: theoretical ingrowth of $^{137\text{m}}\text{Ba}$ given as a fraction of the ^{137}Cs activity as a function of time after separation.	154
Figure 65. Illustration of barium ingrowth in the cesium spectra over eight one-minute counts. Upper-right plot shows the ^{137}Cs x-ray in better detail, while the lower-right plot shows the ^{137}Cs 662-keV peak.	155
Figure 66. Five-minute count of the unseparated AW sample with the CZT detector.	157
Figure 67. Mass chromatogram of an injection of AW to assess elution times of expected radioactive fission products (Nd shown for clarity).	158

Figure 68. Gamma chromatogram of an injection of AW as illustrated in GADRAS with the peaks labeled for comparison to the mass chromatogram.	159
Figure 69. Gamma chromatograms of all three injections of AW visualized in GADRAS to show consistency of elution times.	159
Figure 70. Illustration of background subtraction in GADRAS to acquire CZT spectra as a function of energy.	160
Figure 71. Smoothed, background-subtracted (through GADRAS) Ru spectra from triplicate acquisitions with the CZT, summed from $t = 250\text{--}430$ s in Figure 61. Overlaid (in red) is the summed ruthenium-cesium MCNP simulated spectrum.	162
Figure 72. Smoothed, background-subtracted (through GADRAS) Ce spectra from triplicate acquisitions with the CZT, summed from $t = 780\text{--}960$ s in Figure 61. Overlaid (in red) is the summed ruthenium-cesium MCNP simulated spectrum.	163
Figure 73. Smoothed, background-subtracted (through GADRAS) Eu spectra from triplicate acquisitions with the CZT, summed from $t = 1200\text{--}1290$ s in Figure 61. Overlaid (in red) is the summed ruthenium-cesium MCNP simulated spectrum.	164
Figure 74. HPGe-acquired spectrum of the Ru fraction collected from the AW sample, displayed in log (counts). Major Ru peaks highlighted.	166
Figure 75. HPGe-acquired spectrum of the Ru fraction collected from the AW sample, displayed as linear (counts) to more easily compare to the CZT spectra. Major Ru peaks highlighted.	167
Figure 76. HPGe-acquired spectrum of the Eu fraction collected from the AW sample, displayed in log (counts). Eu peaks highlighted.	168
Figure 77. A diagram illustrating the rapid analytical process (and subsequent timeframes) that could be performed at ORNL for a post-detonation sample with RAPID and an updated inline	

HPGe detector. Green font correlates with an instrument providing a set of data for the sample.
..... 175

Figure 78. The fission yield curves calculated through ORIGEN for an HEU target (blue circles)
compared to a ^{239}Pu target (gray triangles). 187

CHAPTER 1: INTRODUCTION

1.1 Background: Post-detonation Nuclear Forensics

The ability to rapidly analyze nuclear materials, their impurities, and their isotopes produced post-irradiation (i.e. fission products) is important for several areas of research, from basic technology research (technical readiness level [TRL] 1) to successful utility in an operational capacity (TRL 7–9). An example of low TRL research is analysis of short-lived fission products in order to measure nuclear cross-sections, which are instrumental for understanding and predicting nuclear reactions¹. At a higher TRL, tools for rapid material analysis used by war fighters in the field are funded by various Washington D.C. sponsors. Additionally, the current nuclear forensics analytical capabilities of the United States are used to partner with international agencies such as the International Atomic Energy Agency (IAEA)².

Rapid analysis of post-irradiation debris from a nuclear event is very important for the sake of sample attribution, per the Nuclear Forensics and Attribution Act, Sect. 2, enacted in 2010:

“(1) The threat of a nuclear terrorist attack on American interests, both domestic and abroad, is one of the most serious threats to the national security of the United States. In the wake of an attack, attribution of responsibility would be of utmost importance.

4(A) In order to identify special nuclear material and other radioactive materials confidently, it is necessary to have a robust capability to acquire samples in a timely manner, analyze and characterize samples, and compare samples against known signatures of nuclear and radiological material.

(B) Many of the radioisotopes produced in the detonation of a nuclear device have short half-lives, so the timely acquisition of samples is of the utmost importance...”

Essentially, the US government needs rapid analysis of post-detonation material for the sake of attribution and full characterization of the material, including shorter-lived fission products.

1.2 Current Analytical Challenges

An overview of the current analytical techniques being used in nuclear forensics applications is demonstrated yearly during the various collaborative exercises conducted by the nuclear forensics international technical working group. Table 1 lists various destructive analytical techniques that were employed in 2016 analyzing uranium oxide samples. The analytical techniques were also expressed as a function of reporting time (i.e. the time from sample receipt to reporting the data), and as illustrated in Figure 1, it can be seen that most techniques are capable of producing data within one week. This fits the IAEA guideline for analysis timeliness; however, a quicker turnaround (< one week) would be ideal for an analysis of material for attribution in the US, which can be difficult to achieve.

Another challenge of analyzing all of the fission products found within nuclear materials (both post-detonation or others) is their associated matrix: uranium, silica glass, or a mixture of the two (in the case of post nuclear detonation³). Generally, matrices make mass spectrometry analyses more difficult, due to the production of spectroscopic and non-spectroscopic interferences. Here, a spectroscopic interference refers to a matrix ion or compound that overlaps with the analyte of interest in the analysis, which obscures the real signal correlating to the sample. Non-spectroscopic interferences consist of suppression or enhancement of analyte signals through collisions with the ions in the ICPMS plasma which is dependent on the nebulizer flow rate and sampling depths⁴⁻⁶.

Table 1. Summary of the destructive analytical techniques used in the 2016 nuclear forensics exercise².

Analytical technique	# of labs reporting use
Mass spectrometry	13
Inductively coupled plasma – optical emission spectrometry	3
Inductively coupled plasma – mass spectrometry (ICPMS)	6
Graphite furnace – atomic absorption spectrometry	1
Multi-collector ICPMS	3
Thermal ionization mass spectrometry	4
Secondary ionization mass spectrometry	3
Ion chromatography	2

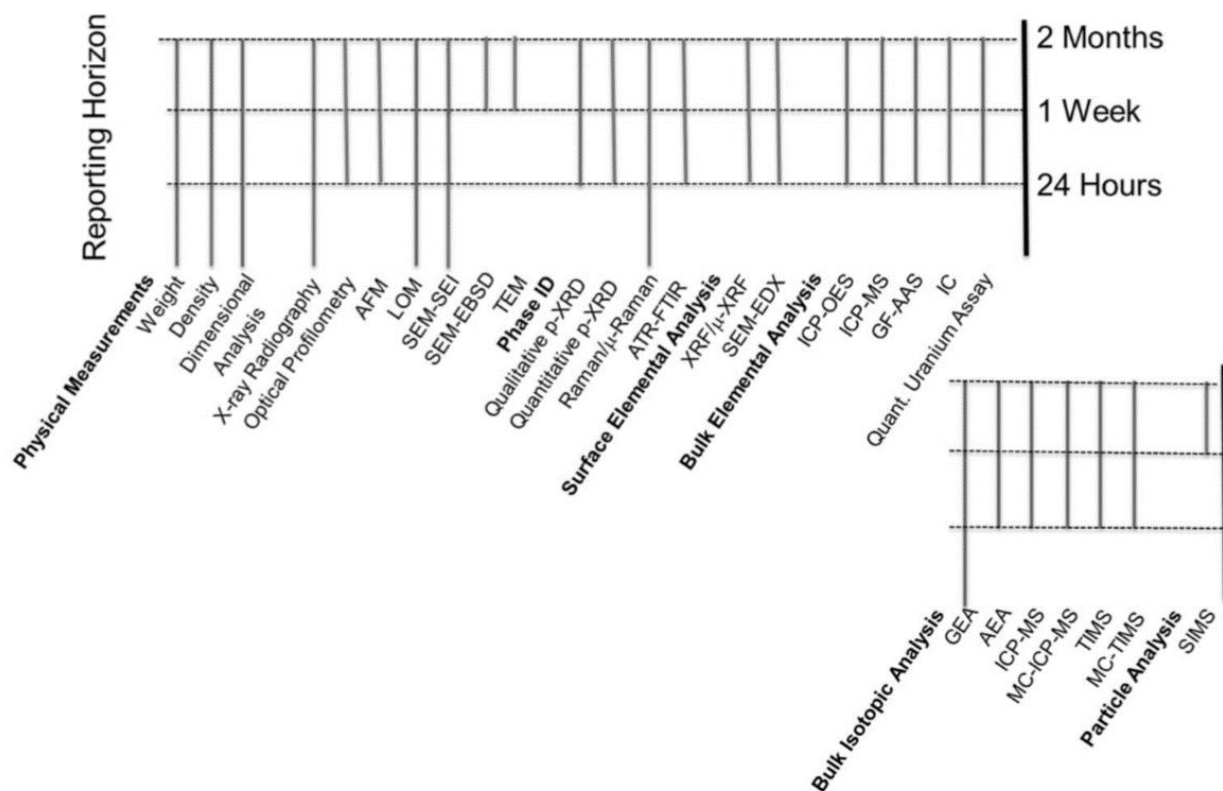


Figure 1. The reporting time horizon for analytical techniques for the 2016 exercise as illustrated by Schwantes² et al.

Due to these complex phenomena, it is advantageous to utilize a robust analytical protocol that is less affected by the matrices.

Lastly, the final challenge in full characterization of the fission products lies within the lanthanide series, which are notoriously difficult to separate due to their chemical similarity and oxidation state⁷. Chapter 2 delves into the available literature and describes the current analytical techniques employed for these samples in various irradiated materials. However, the techniques found in the literature are developed to analyze only one (or a small group of) element at a high level of accuracy; therefore, a technique capable of analyzing a larger number of elements will be more complex.

1.3 The Rapid Analysis of Post-Irradiation Debris Protocol

In order to address all of these challenges, Oak Ridge National Laboratory (ORNL) was tasked to create an operational protocol that utilized chemical separations and mass spectrometry to rapidly analyze as many analytes as possible that would be found in post-detonation debris. The stated scope of work proposed by ORNL for Rapid Analysis of Post-Irradiation Debris (RAPID) was:

“Demonstrate the effectiveness of a rapid measurement protocol which directly couples high pressure liquid chromatography (HPLC) and inductively coupled plasma mass spectrometry. This technique would allow for rapid online HPLC chemical separation with direct isotopic detection and isotope ratio measurements using mass spectrometry and with the incorporation of isotope dilution mass spectrometry, improve accuracy and precision of the analyses over standard elemental and isotopic assay techniques.”⁸

The scope of this research was later narrowed, stating the need to analyze the fission products that would be produced during the detonation, specifically the non-natural isotopes, as most mass

spectrometric techniques cannot analyze these without undergoing chemical separation. Accordingly, this PhD focuses on the development and application of ORNL's RAPID protocol to nuclear forensics.

1.4 Post-Detonation Debris Samples

For this PhD project, two types of surrogate debris created at ORNL and the University of Tennessee, Knoxville (UTK) were utilized to appropriately test the RAPID method for matrix robustness during method development.

1.4.1 ORNL Debris Generation

In order to duplicate the nuclear weapon-generated “melt glass”, a plasma torch system was designed, procured, and set up at ORNL in the Process Engineering Research (PER) group. The theory was to create a representative mixture of dry materials that are expected in the melt glass/debris (e.g. silicon, iron, uranium, and other matrix elements found in soil) and propel it through a plasma torch to simulate the high temperatures generated in a weapon detonation. Ideally, the composition of the matrix should be able to be adjusted to whatever is suitable to the situation simulated (desert vs. urban, uranium vs. plutonium, etc.), which in combination with the HFIR ability to irradiate targets to produce ample fission products, offers a very powerful tool for generating samples for the nuclear forensics community. Figure 2 displays particles typically created by this method.

In 2017, the ORNL debris analysis project received an extension in return for further analysis of this debris: computer models were produced to further understand the physics within the plasma torch during interaction with the sample (i.e. fractionation), and NACIL analyzed the resultant debris to aid in confirmation of the process efficiency. RAPID, offline ICPMS, and gamma

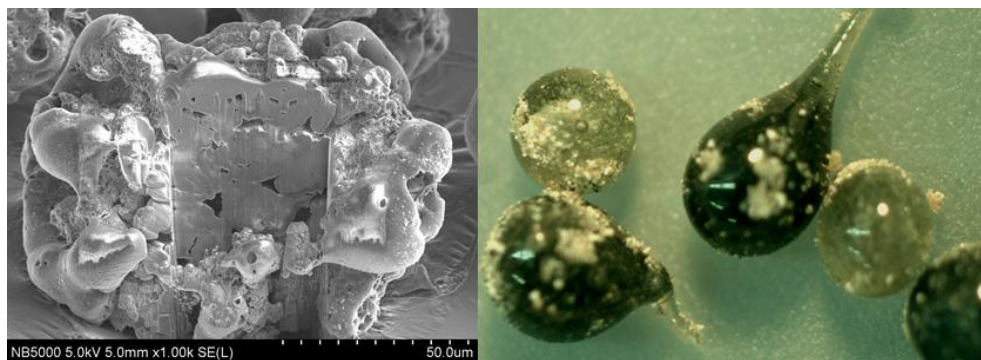


Figure 2. A light microscope image of larger, 1 mm glassy particles (right), and a focused ion beam was used to visualize the inside of a melted surrogate debris particle (left) by the PER group.

analysis were utilized in these measurements. The samples received from this process were a homogeneous loose, powdery material with occasional black glassy particles in the torch runs (TR).

1.4.2 UTK Surrogate Debris Generation

The other type of surrogate debris used for this PhD project included that produced at UTK by several generations of graduate students. It has a similar composition to that of the ORNL debris, but it was created using oxides (in powder form) and melted using a furnace over an extended period of time^{9,10}. Conversely to the ORNL samples, as can be seen in Figure 3, these samples are generally large pieces of glass (~ 1 cm diameter).



Figure 3. Samples of UTK surrogate debris, produced by Giminaro¹¹ et al..

1.5 Dissertation Objective

Rapid and accurate analysis of fission products (especially within nuclear debris) is essential to the nuclear forensics community and as a major component to the attribution cycle in the case of a nuclear event. Any tool or protocol developed that decreases the overall sample analysis timeline in a forensic scenario adds utility. RAPID was developed to analyze a wide breadth of fission products in a short period of time with minimal matrix effects to the analysis and thus fits the criteria to add a useful capability to the nuclear forensics toolkit as a screening tool.

The research question presented for this PhD work was: *how can the RAPID method be improved and developed for useful application to post-detonation nuclear forensics?*

During the course of this project, while analyzing freshly generated fission products, it was realized that an inline gamma detection capability (post-separation, pre-ICPMS) would be complementary to RAPID for these rapid fission product analyses and for additional applications beyond nuclear forensics. This combination of a chemical analysis technique and radiation detection was a perfect opportunity to further this PhD research and test a proof-of-concept system with applications to both fields of chemistry and nuclear engineering.

In this dissertation, the method development of RAPID and the inline gamma detection system are presented, including analyses of irradiated materials for fission product content and surrogate debris for method robustness. Lastly, a final experiment will be proposed, from cradle to grave of an irradiated sample, combining RAPID and other complementary analytical tools in tandem with RAPID for a demonstration of the full capability available here at ORNL for rapid fission product analysis applicable to nuclear forensics.

CHAPTER 2: LITERATURE SURVEY

2.1 Focus of this Review

The Technical Nuclear Forensics (TNF) field vastly evolved this last decade – there are numerous analytical chemistry techniques developed for nuclear materials investigation in case of an event, such as a nuclear weapon detonation, a radiological dispersal device, or orphaned radioactive materials. There are several relevant review papers recently published documenting the advancements of these techniques. Fedchenko¹² provides a survey and an evaluation of the scientific discipline of nuclear forensic analysis, as well as its applications to specific international issues from the 1940's to the present day. Song¹³ et al. discuss the recent developments in nuclear forensics and safeguards analysis using mass spectrometry (MS), including recent publications and applications of the most common MS methods (i.e. thermal ionization, inductively-coupled plasma, and secondary ion). Schwantes² et al. provide a comprehensive review of the fourth Collaborative Materials Exercise completed by the Nuclear Forensics International Technical Working Group (ITWG), where over 30 analytical techniques were utilized to characterize various nuclear materials, ten of which were applied for the first time in an ITWG exercise. Stratz¹⁴ et al. discuss modern advancements in post-detonation nuclear forensic analysis in the last decade, focusing on the creation and rapid analysis of synthetic nuclear melt glass created post-detonation of a nuclear weapon.

This literature review surveys and discusses the destructive analysis (DA) techniques currently utilized for nuclear forensic analysis, specifically involving separation techniques and MS pertinent to post-detonation debris. Lastly, the specific analytical method for this project will be reviewed and discussed at length.

2.1.1 Materials of Interest

The primary material of interest in a nuclear forensic analysis is post-detonation debris, otherwise known as “nuclear melt glass”; however, the only presently recorded melt glass, trinitite, was formed at the Trinity detonation in Alamogordo, NM in 1945. To enable broader analysis and make more varieties of material available, many studies are being performed to design and create synthetic melt glass with necessarily limited methods for validation and verification^{9,10,15}. Subsequently, these studies are accompanied by methods to characterize trinitite and otherwise produced melt glass^{3,16–23}. Analyses include both radiometric and radiochemical techniques, such as alpha, beta, and gamma spectrometry, along with various chemical analysis techniques, which will be discussed in the following sections.

Additionally, vital analyses of actinides and fissions products pose many difficulties and have not been satisfactorily solved for complex, real-world matrices in which melt glass is expected. Experiments performed with materials such as used nuclear fuel often give results useful to the forensic analysis of actinides and fission products^{24–32}. The number of fission products is significant; to illustrate, the fission product spectrum is shown in Figure 4. Of note, it can be seen that part of the fission products falls into the rare earth element (REE) category, also known as lanthanides (shown in Figure 5), and thus are a useful class of elements for forensic scientists. Due to the lanthanides exhibiting very similar chemical properties, characterization of them is non-trivial, as will be covered later in this dissertation.

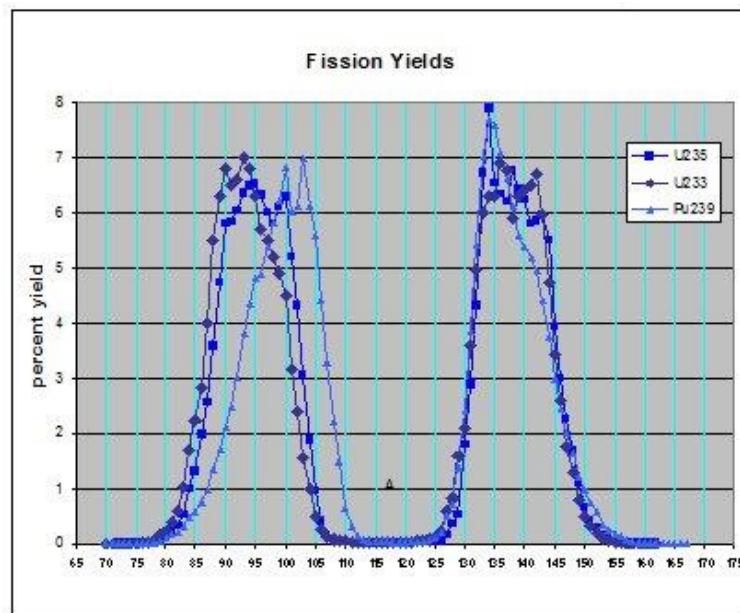


Figure 4. Fission product spectrum as a function of mass number³³

THE PERIODIC TABLE OF ELEMENTS

Symbol Key

Atomic number | Element symbol | Element name

Groups of elements

- s block elements
- p block elements
- d block elements
- f block elements

Colour Key

1 H Hydrogen	2 He Helium																	18 Ar Argon	19 K Potassium	20 Ca Calcium											36 Kr Krypton	37 Rb Rubidium	38 Sr Strontium											54 Xe Xenon	55 Cs Cesium	56 Ba Barium															86 Rn Radon																																			
3 Li Lithium	4 Be Beryllium																	12 Mg Magnesium	13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon	19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton	37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	55 Cs Cesium	56 Ba Barium	57-71 Lanthanides	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon	87 Fr Francium	88 Ra Radium	89-103 Actinides	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson
																																57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium																																																		
																																89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium																																																		

CC BY-NC-ND

© Andy Brunning/Compound Interest 2017 - www.compoundchem.com | Facebook: facebook.com/compoundchem | Twitter: [@compoundchem](https://twitter.com/compoundchem)

This graphic is shared under a Creative Commons 4.0 Attribution-NoDerivatives-NonCommercial licence.

Figure 5. Fission-generated elements (highlighted in orange) and the lanthanides (noted in black square).

2.1.2 Overview of the Sample Analysis Process

The analysis process varies from sample to sample, depending on what the starting material is, what element(s) is being analyzed, and to what extent (i.e. concentration level). Some techniques, such as secondary ionization mass spectrometry or laser-ablation ICPMS, directly analyze solid samples and can provide spatial elemental characterization of the sample. The other destructive analyses all require sample preparation (dissolution, separation, purification) before operation. Lastly, if the element in question only exists in very low concentrations, a high-sensitivity method may have to be used (e.g. multi-collector or sector-field ICPMS). All these items must be taken into consideration before selection of the instrument and subsequent analysis; there are various pros and cons to each technique. Below is an example of a typical sample analysis process from the viewpoint of the analyst:

- 1) What is the sample and what level of analysis is needed?
 - a. What elements are being analyzed?
 - i. Homogenous/bulk or spatial analysis?
 - b. Do these elements need separation from known interferences?
 - c. What concentration do the elements exist in (i.e. how sensitive of an instrument is needed)?
 - d. Is there a matrix that will cause an issue with the analysis or instrument?
- 2) Is there any preparation that needs to be completed before analysis? (This is highly dependent on the instrument chosen)
 - a. Dissolution
 - b. Purification
 - c. Separation of elements (e.g. lanthanides, isobaric interferences)

3) Example/general pros/cons of primary instruments:

a. Pros:

- i. Isotope dilution MS (lower uncertainty)
- ii. Separation capability (higher accuracy in the presence of interferences)
 1. Online (more efficient analysis process, sample goes directly from separation to detection)
 2. Offline (more time-consuming, but multiple, different separations can be performed if necessary for analysis or adequate purification)
- iii. Spatial analysis (e.g. 2-D mapping of a sample)

b. Cons:

- i. Sample preparation – time consuming
 1. Dissolutions can be lengthy processes given a complex matrix (e.g. glass)
 2. Purification/separation consisting of multiple/iterative steps
- ii. Interferences
 1. If no separation is performed or cannot be (solid sample analysis)

Obviously, there can be a lot of overlap between techniques utilizing MS, given the element(s) of interest and the analysis desired; for example, uranium can be analyzed with several different procedures, but complete analysis of the lanthanides requires separation and thus, some level of sample preparation.

Other sections in this chapter will review the various MS techniques in a very broad sense and go into further depth on relevant work performed on nuclear samples pertinent to this research.

2.1.3 Rapid Analytical Techniques for Post-Detonation Nuclear Forensics

One of the main objectives in nuclear forensic analysis is timeliness, thus, the quicker and more efficient the analysis process, the better. Ideally, all necessary analyses should be completed within a few days of the event in order to support time-sensitive law enforcement investigations. Unfortunately, destructive analysis can involve extensive sample preparation, easily ranging from a few hours to a couple weeks. This sample preparation includes dissolution/dissolution of the sample and the successive separation procedure, if any.

Table 2 summarizes the typical completion timescales for different laboratory methods and techniques, compiled by the IAEA in the 2015 guidelines for nuclear forensics. From this, it can be seen that only a fraction of the analytical techniques currently employed for nuclear forensics can deliver results within 24 hours. Of note, Smith³⁴ et al. added radiochemical separations to their summary of these techniques published in 2008. Chemical separations can be tedious, especially when completed offline with several different types of columns; however, it should not take two months to complete these separations with current capabilities.

To further exemplify this analytical timeline, Croudace³⁵ et al. reviewed the general analysis sequences and methods used in investigations of material for nuclear forensics or emergency situations, shown in Figure 6. Once again, separations are determined to be a long-term part of the forensics methodology but necessary for an in-depth characterization of the material being investigated.

Table 2. Laboratory Methods and Techniques with Typical Completion Timescales³⁶

Technique/method	Conducted within:		
	24 h	One week	Two months
Radiological	Dose rate Surface contamination Radiography		
Physical characterization	Visual inspection Optical microscopy	Scanning electron microscopy (SEM) X-ray diffraction	Transmission electron microscopy SIMS <i>Radiochemical separations</i> ³⁴
Isotopic analysis	High resolution HPGe	TIMS ICPMS	
Elemental/chemical composition	X-ray fluorescence	SEM ICPMS IDMS	GC-MS

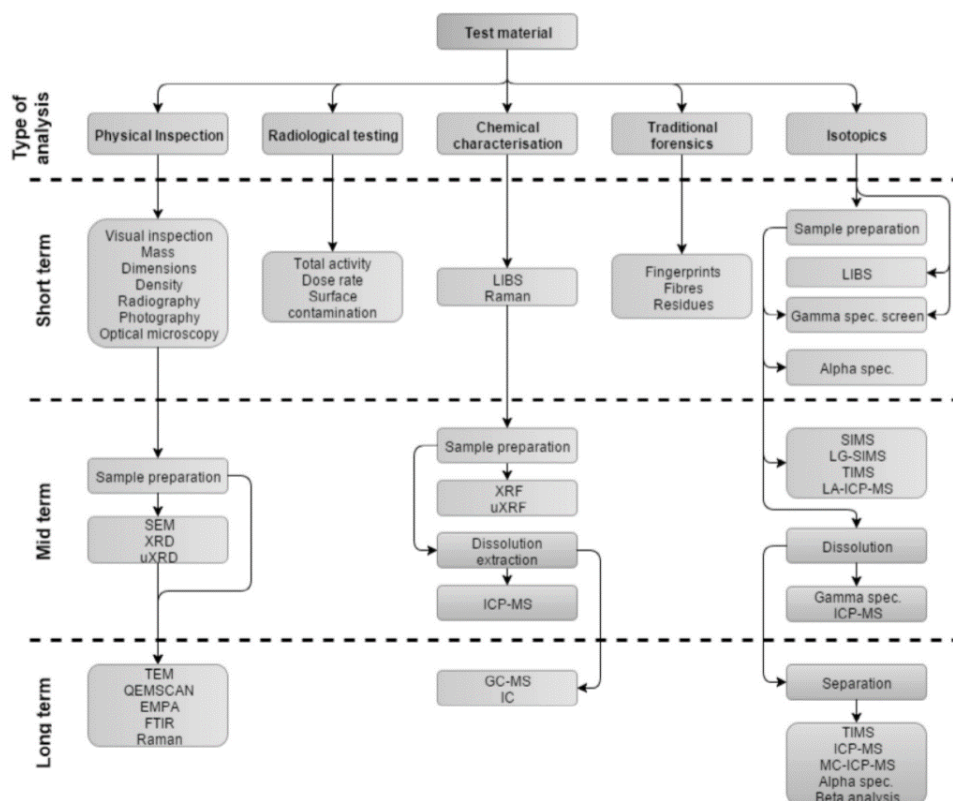


Figure 6. A summary of analytical sequences and methods typically used in the context of nuclear forensics investigations as illustrated by Croudace³⁵ et al.

Recently published work claims rapid analysis developed for nuclear forensics often can deliver results under one week, using various separation and detection schemes. Dustin³⁷ et al. performed a comparison between solution-mode ICP-MS and LA-ICP-MS: good agreement exists between these two techniques. Solution-mode takes around a week, including sample dissolution, whereas LA-ICP-MS takes two min per analysis, nonetheless, a significant number of analyses need to be acquired since each scan ablates a small, relatively homogenous area of $\sim 45\ \mu\text{m}$. Bürger³⁸ et al. designed a rapid isotope ratio analysis screening procedure for solid nuclear material by LA-TOF-ICP-MS, where results can be obtained within an hour.

Maxwell^{39–44} et al. developed several procedures to rapidly analyze various materials (e.g. asphalt, soil, air filters, and concrete) for use in emergency response, utilizing multiple offline column separations and achieving a separation time of around three hours; however, the detection mechanism of alpha spectrometry requires an additional one to sixteen hours.

Generally, a typical analytical protocol for nuclear forensics examinations or emergency response situations focuses on a single element^{45,46}, or a small group (e.g. lanthanides^{47,48} or actinides^{41,49}), to expedite the analysis timeline. When analysis of multiple elements is required, several different protocols are often performed sequentially, depending on the sample preparation techniques.

2.2 Overview of Mass Spectrometry Techniques

2.2.1 Inductively-Coupled Plasma Mass Spectrometry

ICPMS is one of the most widely used MS techniques in analytical chemistry, and it is also the case for nuclear forensic analysis. An inductively-coupled plasma ionizes the sample, which goes into a mass spectrometer for separation and quantification. Its variants include laser-ablation ICPMS (LA-ICPMS), sector field ICPMS (SF-ICPMS), and multi-collector ICPMS (MC-

ICPMS). Normally, ICPMS preparation is quite rigorous, involving dissolution and dilution before analysis; however, laser ablation can eliminate this need for sample preparation, thus directly ablating the sample material for transportation into the ICPMS. Also, generally, SF-ICPMS utilizes magnetic fields rather than a quadrupole to aim for higher resolution and lower limits of detection, while MC-ICPMS uses multiple detectors for higher resolution and detection efficiency, all at the cost of a higher price tag. The main disadvantage of ICPMS is the amount of isobaric or polyatomic spectral interferences. Examples of polyatomic interferences are listed in Table 3.

To give the reader a glimpse of how saturated the analytical chemistry realm is with papers using ICPMS on the types of samples pertinent for this dissertation, the following paragraphs will list recent research performed on samples for forensics, nuclear fuels, and other relevant materials.

There have been several recent papers published on the use of ICPMS for nuclear forensic analysis within the last five years. Varga⁵⁰ et al. discuss the use of ICPMS for a rapid determination of the production date of plutonium for nuclear forensic purposes by isotope ratio analysis. Similarly, Miyamoto⁵¹ et al. determined the age of individual uranium-plutonium mixed particles, with various ratios, from certified reference materials. Marin⁵² et al. utilized LA-SF-ICPMS for the rapid determination of uranium isotopes in various enriched uranium samples. Meyers⁵³ et al. investigated the forensic signatures from two former uranium-processing facilities using chemical purification and MC-ICPMS.

Saha⁵⁴ et al. analyzed the trace impurities in metallic nuclear fuels with time-of-flight ICPMS. Shi⁵⁵ et al. quantified various actinides (uranium, thorium, and plutonium) in nuclear waste and fuel with ICPMS. Joe²⁶ et al. determined neptunium content in both synthetic and spent fuel samples, using isotope dilution mass spectrometry and ICPMS.

Table 3. Examples of ICPMS Interferences⁵⁴

Isotope	Natural Abundance (%)	Possible Polyatomic Interferences
¹¹⁴ Cd	28.73	¹¹⁴ Sn, ⁹⁸ MoO
¹¹⁵ In	95.71	¹¹⁵ Sn
¹⁴⁶ Nd	17.189	¹³⁰ BaO
¹⁵¹ Eu	47.81	¹³⁵ BaO, ¹³⁴ BaOH
¹⁵³ Eu	52.19	¹³⁷ BaO
¹⁵⁸ Gd	24.84	¹⁵⁸ Dy, ¹⁴² CeO, ¹⁴² NdO
¹⁵⁹ Tb	100.00	¹⁴² CeOH, ¹⁴³ NdO
¹⁶⁴ Dy	28.26	¹⁴⁸ NdO, ¹⁴⁸ SmO

Additionally, methods for age dating or origin analysis have been developed using both ICPMS^{56,57} and SF-ICPMS^{58,59}, as well as for treaty verification⁶⁰. Circa 2010 and earlier, other papers describe use of various types of ICPMS to analyze uranium, plutonium, and thorium, in samples such as IAEA swipes⁶¹, soil^{39,62–67}, nuclear fuel^{27,68–70}, and uranium oxides⁷¹, as well as materials after neutron irradiation⁷².

2.2.2 Secondary Ionization Mass Spectrometry (SIMS)

SIMS is largely used for particle analysis in nuclear forensics and operates by using an ion beam focused on the sample – a solid or thin film – to produce secondary ions, which are then analyzed in the mass spectrometer. It is a very sensitive surface analysis technique; however, due to the large variation in ionization probabilities in materials, quantification of samples can be difficult. Variants on SIMS for nuclear forensic analysis include large-geometry (LG-SIMS), time-of-flight (TOF-SIMS), and sector field (SF-SIMS). Large geometry allows for a higher mass resolution than normal SIMS, while the TOF-SIMS has many advantages over SIMS including high mass resolution, large mass range, and high sensitivity. General disadvantages of SIMS comprise of cost, varying secondary ion yields, matrix effects, reactive surface contaminants, and others, most

of which TOF-SIMS can overcome. There are various SIMS methods developed for nuclear forensics applications^{73–80}.

2.2.3 Thermal Ionization Mass Spectrometry (TIMS)

TIMS involves vaporization and ionization of the sample, which is then loaded on a filament and ionized by resistive heating. Ideally, the sample should be chemically pure, in order to limit the amount of impurities present, which can be completed using chemical separations (e.g. extraction chromatography). Internationally, TIMS has been recognized as the gold standard for data analysis of isotope ratios and concentrations, especially uranium and plutonium. The most common variant on TIMS is the addition of isotope dilution mass spectrometry, the concept of which will be discussed in more detail in a later section. Aggarwal⁸¹ recently published a review paper on TIMS and its numerous applications, including several developments in nuclear forensics.

The main application of TIMS in nuclear forensic analysis is for radio-chronometry, or the calculation of the age of a material based on unique parent-daughter couples (e.g. ^{235}U - ^{231}Pa , ^{239}Pu - ^{235}U , ^{241}Pu - ^{241}Am)⁸². Additionally, certain isotope ratios (e.g. elements Cs, Sr, Nd, Pb) can be used to trace the origin on the material due to unique material processing characteristics. Several methods to measure such isotope ratios have been developed^{83–91}.

2.3 Chemical Separation Techniques

2.3.1 Chemical Separations Overview

As mentioned earlier, a large portion of samples require a chemical separation process in order to obtain highly accurate isotopic results necessary for nuclear forensic analysis. This section will describe the most prevalent chemical separation techniques used for those analyses, including

analysis of actinides and fission products. Ion chromatography will be covered in detail in the next section.

High pressure liquid chromatography (HPLC) is a common analytical technique used to prepare samples for mass spectrometric analysis. HPLC uses two phases, a mobile phase (which includes the sample) and a stationary phase (resin, beads, etc.) – as the sample moves down the pressurized column, the compounds/elements travel between the mobile and stationary phase at various rates: this is what drives the separation. Different stationary phases can be chosen to specifically target certain species to separate (e.g. cations, trivalent actinides, organic species, etc.). Both extraction chromatography and ion chromatography are variants of HPLC.

Extraction chromatography (EC) uses the selectivity of a liquid-liquid extraction but produces a chromatogram. Separations occur based on the distribution of cations (or anions) of interest between an organic and aqueous phase. The stationary phase is the selected extractant, which is the organic liquid/phase adsorbed onto an inert support – thus, movement of the cation from the mobile to the stationary phase involves a transition from the aqueous phase to the organic phase. For example, extractants for actinide separations typically include TEVA, TRU, and DGA resins. The different Eichrom resins and the corresponding selectivity is listed below in Table 4. Of note, there are additional resins used for nuclear forensics applications that are not Eichrom, but the process and timeline are similar.

Correspondingly, many methods have utilized these resins to separate elements of interest in several relevant applications: nuclear forensics^{20,92–95}, age dating^{96–99}, radioactive waste analysis^{100–102}, and various emergency environmental situations^{40,43,103–106}.

Table 4. Eichrom Resins and Selectivity¹⁰⁷

Material	Selectivity
TRU Resin	Actinides(III, IV, VI), Ln(III)
UTEVA Resin	U(VI)
TEVA Resin	Th(IV), Np(IV), Pu(IV), Tc(VII))
Sr Resin/Pb Resin	Sr, Pb
Ln Resin	Ln(III)
Actinide Resin	Actinides

Other miscellaneous, less well-characterized separation techniques developed for nuclear security applications utilize gas chromatography¹⁰⁸, liquid-liquid extraction¹⁰⁹, EC paired with extraction by triazine ligand¹¹⁰, ultrasound-assisted acid leaching¹¹¹, and electrochemically-modulated separations¹¹².

2.3.2 Ion Chromatography (IC)

Ion (or ion-exchange) chromatography has been commonly used for actinide and fission product separations since the 1980's – it is a versatile, sensitive, and selective technique for determination of various cations and anions at ultra-trace levels. Previous applications include ionic analysis in pharmaceutical, industrial, food, and environmental samples. Ion exchange chromatography separates based on charge; that is, cation exchange separates molecules which are cations, and anion exchange separates anions. Once bound in the stationary phase, these molecules can be eluted by an eluent containing a higher concentration of ions or by changing the pH of the column. Once the molecules of interest elute, a detector is needed to characterize and quantify them – several types of mass spectrometers can fulfill this requirement, as well as radiation detectors. A typical HPLC/HPIC schematic diagram is shown below in Figure 7.

Most relevant to this research, Badaut¹¹³ et al. applied IC to study common inorganic anions in uranium ores of different origins, observing clear differences between mines. Another forensic

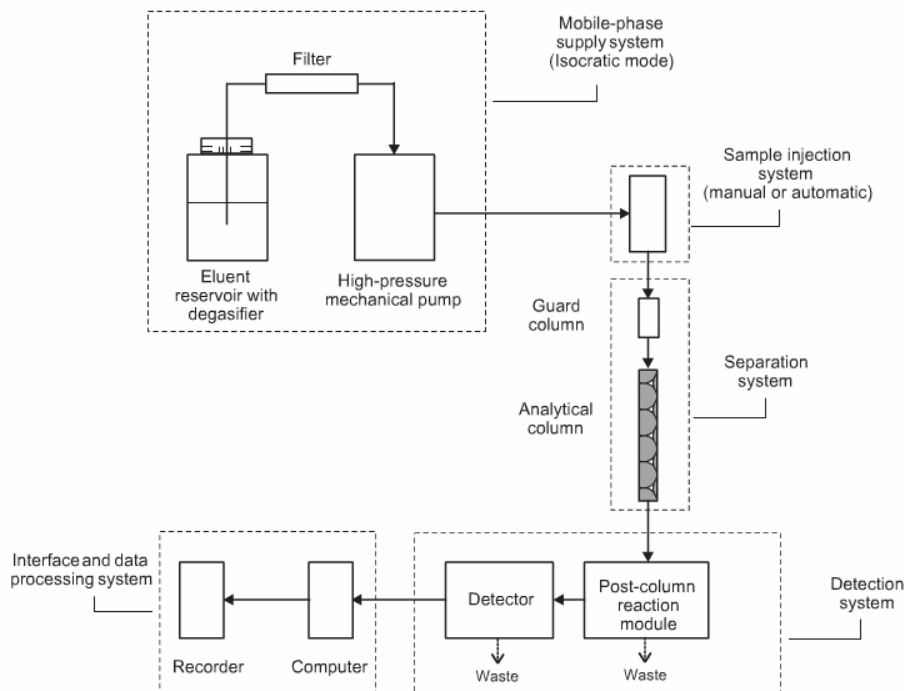


Figure 7. An HPLC Schematic Diagram¹¹⁴

investigation analyzed a plutonium reference material by age-dating, utilizing ion-exchange resin for separation and ID-TIMS for detection¹¹⁵.

Many combinations of IC and various (non-ICPMS) detection mechanisms ranging from scintillation detectors to photo-diode arrays to fraction collection have been applied to samples needing separation of actinides/lanthanides from miscellaneous matrices through the years^{116–125}, demonstrating the versatility of IC.

2.3.2.1 Ion Chromatography-ICPMS (IC-ICPMS)

Ion chromatography coupled with an ICPMS separates and subsequently detects trace-level quantities of elements from various matrices, such as environmental samples, nuclear waste, and uranium ore. Generally, this coupling of IC and ICPMS can either be online (direct coupling of the output of the IC to the input of the ICPMS) or offline (fraction collection or additional

processing occurs after separation before detection). Figure 8 illustrates a simple schematic of both off- and on-line experimental setups. Clearly, online analysis is faster and overall more efficient than its offline counterpart; however, both configurations remain present in modern research studies. This coupling concept is not new: Almon¹²⁶ et al. introduced the procedure of analyzing fission products and actinides in nuclear waste using online IC-ICPMS beginning in 1991.

Offline IC-ICPMS separations include analyses of cesium^{127,128}/plutonium^{129–131} in environmental samples, uranium¹³², PuBe sources¹³³, and various metals in nuclear waste¹³⁴. More prominently, online techniques developed for IC-ICPMS examined analyses of: actinides in uranium leachate¹³⁵, spent nuclear fuel^{27,30,136–140}, and environmental samples^{141,142}; iodine in groundwater¹⁴³; fission-generated lanthanides in high burnup fuel¹⁴⁴; and metals in bio-materials¹⁴⁵.

SF-ICPMS and MC-ICPMS detectors produce variations on the IC-ICPMS couplings. Online IC-SF-ICPMS methods were developed to determine strontium levels in bones/soil samples¹⁴⁶ and industrial ores¹⁴⁷, as well as actinide content in environmental samples¹⁴⁸ and iodine in arctic snow¹⁴⁹. Additionally, online IC-MC-ICPMS was used to measure strontium ratios in environmental samples^{150–152}, neodymium ratios in nuclear fuel samples¹⁵³, and magnesium ratios in water/rock samples¹⁵⁴. Of note, Eppich¹⁵⁵ et al. utilized IC and MC-ICPMS in an analysis of fallout melt glass, presenting the actinide composition from a near-surface nuclear detonation.

In 2011, Michalski¹⁵⁶ et al. published a review article on the analysis of various metals and halides with IC-ICPMS, reporting low detection and quantification limits for this technique and specific analyte/eluent combinations.

Lastly, several DOE national laboratories completed two round-robin exercises comparing the performances of various analytical techniques (IC, EC, ICPMS, TIMS). The first one

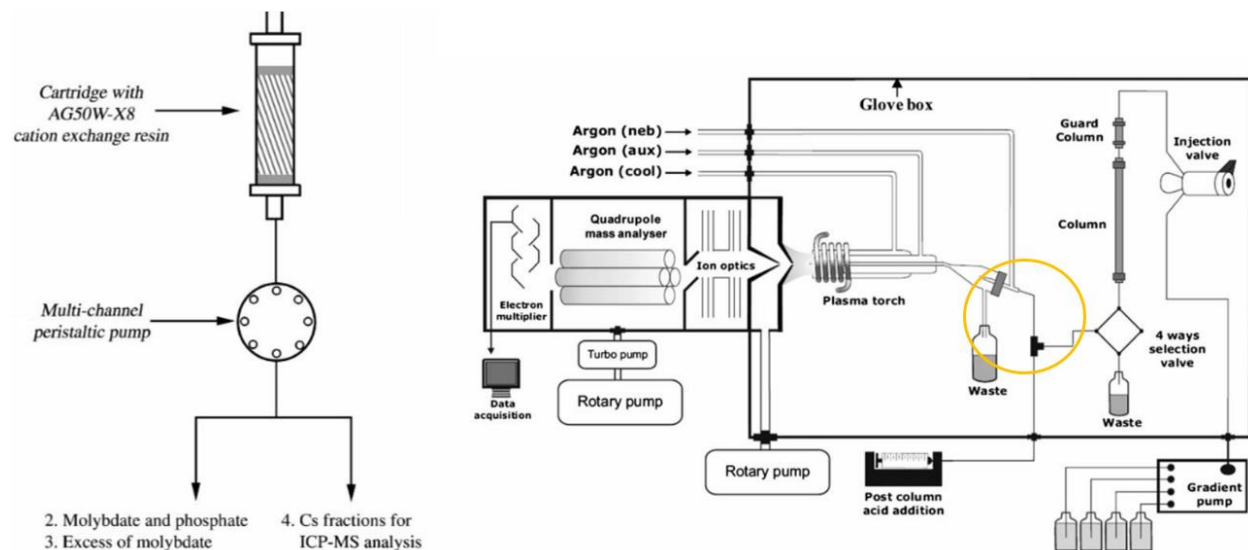


Figure 8. Examples of offline¹²⁷ (left) vs. online¹⁵⁷ IC-ICPMS (right) schematics

determined the concentration of various plutonium isotopes in NIST-certified soil¹⁵⁸ and the other measured the uranium and plutonium content in environmental swipe samples¹⁵⁹. These round-robin exercises demonstrate that several analytical techniques can be utilized in tandem to successfully characterize nuclear materials; however, the more techniques used, the longer the time needed for the full analysis.

Of note, the use of isotope dilution MS (IDMS) is commonly implemented to obtain lower uncertainties in analyses (this will be discussed further in a later chapter) – several IC-ICPMS methodologies document this usage for fission product/actinide analysis^{28,157,160–162}.

2.4 Inline Radiation Detectors

In general, most radiation detection techniques are non-destructive, which is preferable for rapid analytical protocol in some situations (i.e. nuclear forensics, neutron activation analysis,

safeguards treaty verification). However, it can be advantageous to have the capability of analyzing nuclear emissions as part of a process, otherwise known as an inline system.

Historically, the main advantage of implementing an inline detection system is to monitor a process without disruption, such as nuclear fuel reprocessing. In this example, instruments include gamma, alpha, and neutron detectors for rapid and continuous observation of gamma activity used for uranium and plutonium monitoring of a 1950's reprocessing facility¹⁶³. Other applications include monitoring environmental radon¹⁶⁴, nuclear fuel cycle facilities^{165,166}, and radionuclides in waste water^{167,168}. Another advantage of coupling radiation detection and destructive chemical analysis is the ability to chemically separate elements which could cause spectral interference in a gamma spectrum. Recent work on this front utilized chemical separation to lower minimum detectable activity limits for neutron activation analysis of several transition metals^{169,170}; however, the separation mechanisms and gamma detectors were not directly coupled. Other, older work applying chemical separations before gamma analysis include an automated radioimmunoassay system employing a charcoal-Dowex column and a NaI detector¹⁷¹ and a methodology to reduce interferences from NAA samples of environmental samples with an anion exchange procedure¹⁷².

CHAPTER 3: THEORY

3.1 Scope

Generally, it is a non-trivial task to fully understand the quantum mechanical aspects of chemical separation and ligand exchange reactions^{173,174}; often, super-computers are utilized to model systems of one element and one chelating molecule¹⁷⁵. Due to the complexity of the separation employed for RAPID—four eluents, two ion exchange resins, and varying sample matrices—it was not a task for this PhD to completely characterize and understand all the various separation processes. However, it was still necessary to learn and comprehend a basic level of chemical separation science and generally know the processes involved in this research.

This chapter will underline the basic chemical processes and radiation detection physics exploited for this project.

3.2 Overview of Basic Chemistry Principles

3.2.1 Lanthanide Properties

It is well known that lanthanide separation is a complex task due to their chemical similarity. This is partly due to a phenomenon named the lanthanide contraction: instead of the expected growth in ionic radius across the lanthanide series, the opposite occurs, and the radii decrease. The majority of the lanthanide elements exist in a trivalent state (i.e. an oxidation state of +3) in aqueous solutions – this is the chemical property that is exploited to chemically separate this group of elements.

There are several ways to separate the lanthanides: chemical separations, ion exchange methods, and solvent extraction. Chemical separations operate on oxidation state differences, so only

elements existing in a non-trivalent state (i.e. Ce^{4+} , Eu^{2+}) can be separated this way. Ion exchange chromatography separates the lanthanides via a cation or anion exchange resin, and their subsequent elution order is dependent on charge density (cation system: reverse atomic number order $\text{Lu} \rightarrow \text{La}$; anion system: $\text{La} \rightarrow \text{Lu}$). Unfortunately, this separation is not very efficient when scaled to the commercial level, which leaves solvent extraction as the main large-scale option. Solvent extraction, using multiple stages, uses two phases (organic and aqueous) to separate the heavier lanthanides from the lighter ones; heavier lanthanides tend to form complexes that are more soluble in the aqueous phase. Depending on the final usage (chemical use vs. electronic use), ion exchange can be used for final purification to a 99.999% purity level⁷.

3.2.2 Uranium Solution Properties

Like the lanthanides, quite a few of the actinide elements are also stable in a trivalent state (i.e. transuranium elements beyond plutonium) and thus can be separated by a similar system. Unfortunately, that is not the case for uranium: in solution, it is most stable in a hexavalent state. Separation of uranium from nuclear fuel has several well-known solutions, the most commonly implemented technique using tributyl-phosphate as the organic phase in a solvent extraction process¹⁷⁶.

For this project, the purpose of separating uranium was to eliminate it as a matrix from its daughter fission products. It adheres to the ion exchange column, then can be stripped by a strong acid.

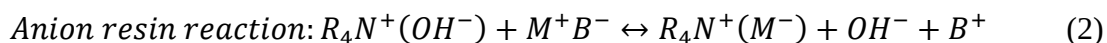
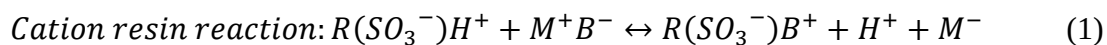
3.2.3 Separation Chemistry

Due to the trace-level analyses performed in this research, it was necessary to keep all chemicals trace-pure, including by recrystallization of acids which had significant levels of contamination in the elements which were being analyzed. Recrystallization will be discussed later in this chapter.

The eluents used include: PDCA (pyridine-2,6-dicarboxylic acid, C₇H₅NO₄); oxalic acid, (C₂H₂O₄, +2H₂O if di-hydrate, aka recrystallized); DGA (diglycolic acid, C₄H₆O₅); and deionized water. Both oxalic acid and DGA were recrystallized, starting in 2018, to lower the concentration of various metal contaminants (mainly cerium) which increased baselines for those elements during analysis. For later analyses, HCl was added at the end of certain runs to strip the uranium off and keep the column “clean” – when this was done, the PDCA was not used, as only four eluents can be managed by the HPIC system. Of note, the pH and concentration of each of these eluents is key for successful separations.

The column used for this research was a Dionex CS5A (with its guard column CG5A), which has both cation exchange (sulfonic acid, R(SO₃⁻)H⁺) and anion exchange (alkanol quaternary ammonium, R₄N⁺(OH⁻)) sites. It was selected for its dual-use capabilities to separate both transition metals and lanthanides with the same separation scheme.

Ion exchange chromatography operates on the basis of ionic interactions between the analyte complex and the column resin: cation exchange resins retain positively-charged cations with a negatively-charged functional group, and anion exchange resins retain negatively-charged anions with a positively-charged functional group. In the case of the Dionex column mentioned above, where M and B are ions in the system for separation:



The functional group for the cation resin is negatively-charged sulfonate and a positively-charged quaternary ammonium group for the anion resin. The ions will exchange based on whichever is the more stable complex; for example, if it is more stable in its nitrate form, it will not adhere to

resin and move off the column more quickly. However, if it adheres to the resin, it needs an eluent which will provide it a preferable complex to elute it off the column. The concentration of eluent is also a factor, in addition to type of eluent, in this distribution of ions between the resin and solution, so manipulations of the concentration can yield different levels of separation. This constant shift in equilibrium is very complex, especially given a large number of ions and several different possible complexes for each ion because of the use of multiple eluents. Figure 9 shows the process each ion traverses in the RAPID process and the possible chemicals it can choose to complex with along the way. It was not a goal of this PhD project to predict exact species of each element as they elute from the column – this diagram is shown to illustrate the complexity of the separation process that RAPID utilizes. Without an additional detector capable of analyzing molecular structure (e.g. electrospray ionization MS¹⁷⁷), the exact species of each complex can be postulated but cannot be confirmed.

The separation scheme used for this project was based on a method developed by Dionex¹⁷⁸, which combined two separations: first, the transition metals form stable complexes with the PDCA and subsequently elute, and next, the lanthanides elute with a combination of oxalic acid and DGA. Due to the difference in oxidation states of the transition metals in the buffered media (+1, +2) and the lanthanides (+3), the lanthanides do not complex with the PDCA, creating a good separation between the two sets of elements. The lanthanides separate by utilizing the selectivity of each lanthanide with oxalate: the strongest complexes formed are the most negatively-charged (and highest surface charge density), thus the elution order is La → Lu. Figure 10 illustrates a resulting separation published by Dionex with this method.

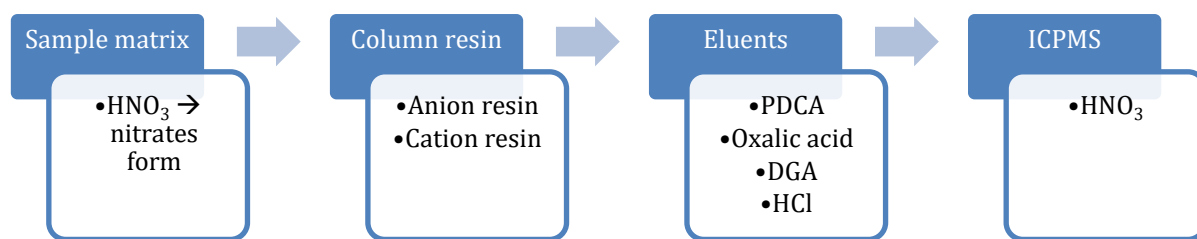


Figure 9. Potential chemical interactions at each stage for each ion going through the RAPID process.

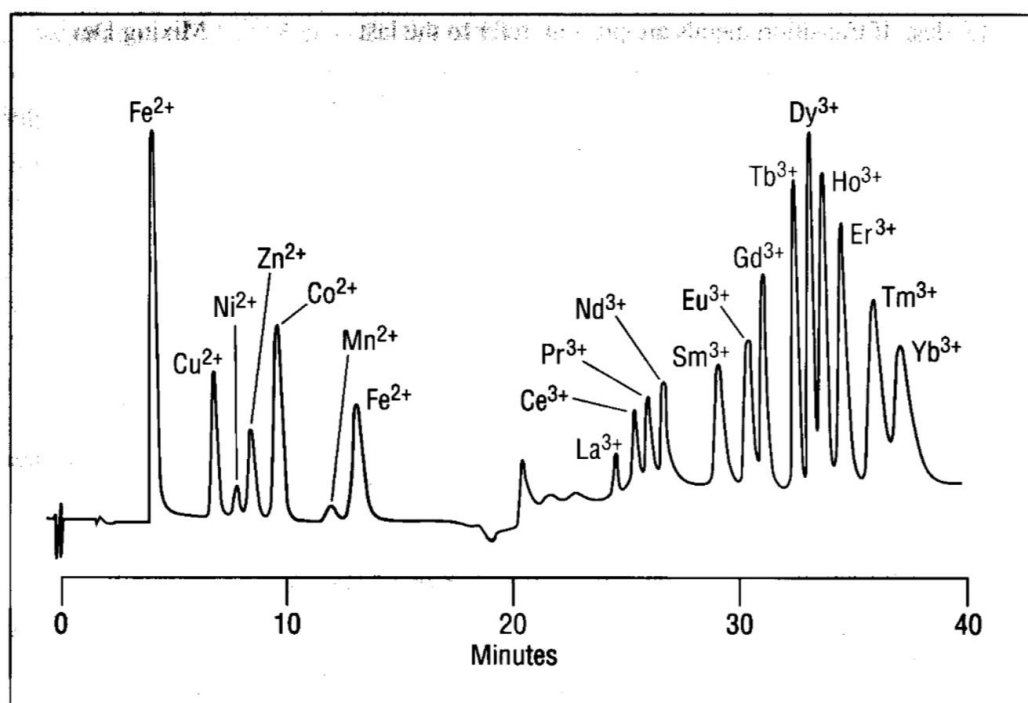


Figure 10. Dionex separation of transition metals and lanthanides in a single injection by IC¹⁷⁸.

3.2.4 Quadrupole ICPMS

3.2.4.1 General Theory

This section is based on a review article by Linge¹⁷⁹ et al. The main principle of ICPMS is elemental differentiation based on atomic mass – while atoms of the same element may have different atomic masses, the isotopic composition of each element is well studied and easily predicted. Because mass spectrometry cannot differentiate between neutral atoms, each atom must be ionized (forming positively charged particles by the removal of an electron), and this process is performed with an inductively-coupled plasma in ICPMS.

A simple schematic of an ICPMS with a quadrupole mass filter is shown in Figure 11. The generalized steps that a sample goes through are:

- 1) The sample is prepared into a suitable form for introduction into the system
- 2) The sample is introduced into the system and ionized in the plasma
- 3) The generated ions are extracted from the plasma
- 4) The ions are focused and transported to the mass filter
- 5) Ions are separated by their mass to charge ratio (m/z) by the mass filter
- 6) Ions are counted/detected to quantify the amount of each in the original sample

Various sample introduction techniques have been developed for ICPMS (solids, liquids, and gases) over the years since its introduction in the 1980s, however, liquid is the most common sample type analyzed with ICPMS and will be the only one discussed in this section. Due to the instability of the plasma, only small volumes of the sample can be introduced at a time as to not extinguish the ICP. This is typically performed with a nebulizer, which disperses the solution as a fine, gas-borne aerosol, and a spray chamber removes the larger droplets from the generated

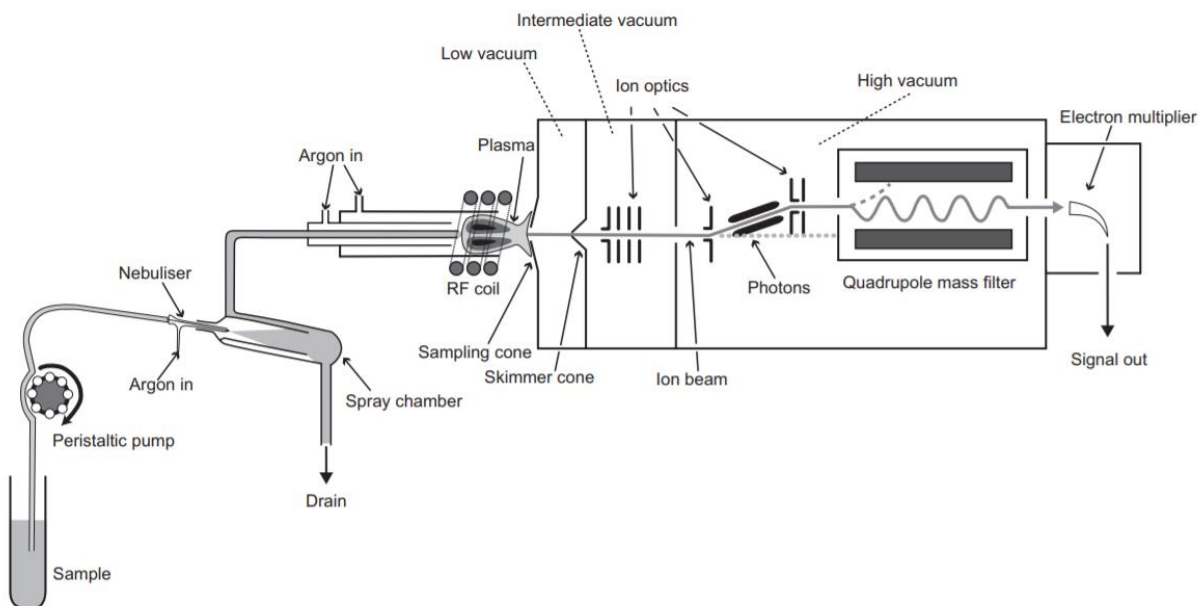


Figure 11. Schematic diagram of the major components of an ICPMS quadrupole instrument as illustrated by Linge¹⁷⁹ et. al.

aerosol. The most common nebulizers are pneumatic, forming an aerosol through a high-speed gas flowing over the tip of a small orifice, and various types of nebulizers have varying efficiency, sensitivity, and resistance to blockage. The type of nebulizer selected depends on the experiment being performed and includes micro-flow and high-efficiency nebulizers (compared to a conventional nebulizer). Some nebulizers self-aspirate without external pumping, but most are used in conjunction with a peristaltic pump, which ensures a constant flow of liquid/sample (unaffected by the sample's viscosity). Unfortunately, any pumping instabilities may introduce noise into the system, and thus the best practice to minimize this effect is to use narrow-bore tubing for sample introduction and to replace it often before it is damaged or flattened. Lastly, in addition to filtering the unsuitably large droplets produced by the nebulizer, the spray chamber serves a second function, removing any solvent from the aerosol, which improves the ionization efficiency and further protects the plasma.

Once the nebulizer converts the sample to a usable aerosol, the second step is sample ionization within the plasma. A plasma is a highly ionized gas (composed of electrons, ions, and neutral particles), and an ICP specifically is a plasma created and maintained by time-varying magnetic fields. Argon is the gas most appropriate for use for an ICPMS due to its inert properties and its ionization energy of 15.2 eV (most elements have an ionization energy $<15 \text{ eV}^{180}$); however, this high ionization energy does inherently create many doubly-charged ions. The quartz torch supports the ICP within three concentric tubes and is mounted inside a (water-cooled) copper coil that provides the magnetic field for the plasma. An alternating current is generated within the coil by a radio-frequency generator (typically 1000–1500 W) and induces an intense electro-magnetic field around the tip of the torch. Two flows of argon gas are produced, between the outer and middle tubes ($\sim 15 \text{ L/min}$) and the middle and central “injector” tubes ($\sim 1 \text{ L/min}$) respectively, and then a high-voltage spark is generated, producing free electrons that are accelerated into the magnetic field, causing collisions and ionizing the argon gas, creating the plasma at the open end of the torch. Next, the sample is introduced to the plasma through the injector tube in droplets, then the droplets are de-solvated and vaporized into a gas, atomizing compounds, and finally, ionizing each individual atom. Optimization of this ionization process can be performed by adjusting the nebulizer, the two plasma gas flow rates, the radio-frequency power supplied to the plasma, and the torch position. The highest signal is created when the energy for ion production (r-f power) is appropriately balanced against the dwell time of the aerosol in the plasma (gas flow rates).

Next, extraction of the ions from the plasma into the high-vacuum region of the ICPMS is completed through two sequential cones, a sampler cone ($\sim 1 \text{ mm}$ diameter orifice) and a skimmer cone ($\sim 0.4\text{--}0.7 \text{ mm}$ diameter orifice). The sampler cone is directly in contact with the plasma, and the distance between the torch and the sampler cones can be adjusted to change the region where

the ions are sampled from. After the plasma gas passes through the sampler cone, it expands into a supersonic jet due to the pressure drop between regions and then enters the skimmer cone, which is located directly behind the sampler cone. Both cones are typically made of nickel or platinum and need to be cleaned (or replaced) regularly, as residue from long periods of operation may build up around both cone orifices, changing their geometry and subsequently affecting ion extraction from the plasma.

Next, the ions must be transmitted from the cones to the mass filter – this is done through lenses, typically a series of metal rings, each with a different voltage. This “lens stack” is in a high-vacuum region located immediately after the skimmer cone’s intermediate pressure region, which effectively pulls the ions from that interface region. The design and arrangement of the lens stack affects the exact dependence of the signal on each lens voltage; however, the lens stack removes neutral species and photons that would create noise on the detector if not eliminated. Once the ions transverse the cones and reach the lens stack, a mass-dependent response is created between the lens voltages and the ions. The voltages cannot be optimized to transport all ions with the same efficiency, so generally, they are optimized to give maximum sensitivity to mid-range mass isotopes ($\sim m/z$ of 125), losing efficiency on the lower and higher mass ranges. Additionally, the “space-charge” effect dictates a maximum number of ions that can be compressed into an ion beam at one time due to mutual repulsion of positive charges of the ions. This causes the lighter ions to deflect away from the ion beam (more so than the heavier ions), and a heavier matrix can exacerbate this effect, further depleting the lighter ions in the beam.

After transmission using the lens stack, and before the detector, the ions are separated by the quadrupole mass filter as a function of their m/z . The mass filter is comprised of four metal rods (see Figure 12), and each opposing rod pair is electrically connected with a DC offset voltage is

applied across each pair. When ions travel in between the rods, the voltages cause the ions to oscillate (as a function of its mass and charge), and large oscillations result in ejection of the ion from the quadrupole. Thus the rod voltages are optimized to allow only a single m/z through the quadrupole at a time, and this filtering system switches very rapidly (can range from 0 to 300 amu in ~ 100 ms) to separate each m/z of interest in the sample. The quadrupole is operated (and maintained even when the MS is not operating) at a high vacuum to protect the quadrupole and limit any interferences within the mass filtering process.

Lastly, the ions that exit the quadrupole mass filter must be counted in order to quantify each m/z in the sample. Each ion is converted to a discrete electrical pulse, and the number of pulses is related to the number of analyte ions present in the sample and, by comparison to a calibration reference sample, converted to an absolute concentration. There are two main pulse counting detectors used in most ICPMS instruments: the channel electron multiplier and the discrete dynode electron multiplier. Both detectors utilize electron multiplication, where each ion hits the detector

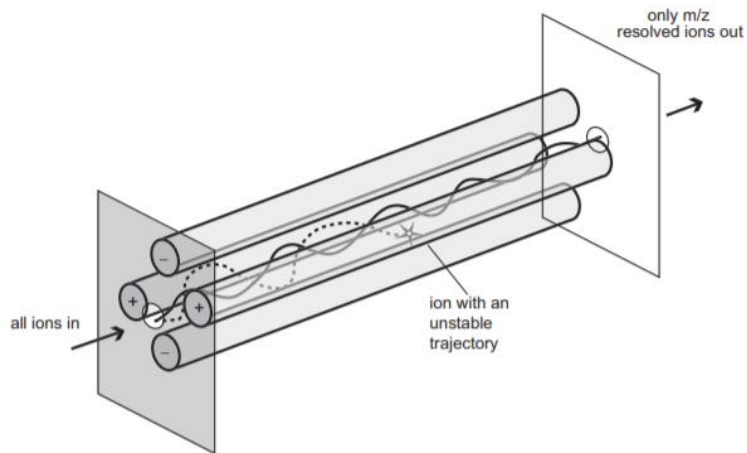


Figure 12. A schematic diagram of a quadrupole mass filter, as illustrated by Linge¹⁷⁹ et al. Voltages are applied to the rods (positive and negative as shown) in such a way that only ions with a single m/z have a stable path and exit the quadrupole.

and forms secondary electrons, until a discrete pulse (of a very large number of electrons) is registered. However, the number of counts registered by the detector is limited by its respective “dead time” (typically ~20–30 ns), where an ion is not counted if it interacts with the detector while the previous ion is in its electron multiplication process. Fortunately, for high ion count rates when this is an issue, this dead time can be used to correct for the missed ion-detector interactions. Typically, most pulse counting detectors are linear between zero and one million counts per second – more modern quadrupole ICPMS instruments have a dual-stage detector that measures ions as an analog signal when count rates become high.

3.2.4.2 Thermo iCAP-Q¹⁸¹

The specifics of the ICPMS (Thermo Fisher Scientific iCAP-Q) used for this research will be presented in this section. The iCAP-Q schematic is illustrated in Figure 13, where:

- 1) sample introduction
- 2) interface (ion generation)
- 3) ion optics/focusing
- 4) mass analyzer

The sample introduction system is comprised of a peristaltic pump, the nebulizer, a Peltier-cooled spray chamber, and the torch with an injector. The peristaltic pump can either be used purely to drain to waste (regular off-line ICPMS) or to draw the sample to the nebulizer in addition to draining to waste (typically used while connected to the HPIC). The iCAP-Q’s nebulizer is made of perfluoroalkoxy, while the spray chamber and injector (inner diameter of 2.5 mm) are both made of quartz. Figure 14 shows the sample introduction system with the nebulizer (1), spray chamber (2), injector (3), and torch (4) labeled, in addition to a separate view of the torch and injector (normally the injector sits concentrically within the torch).

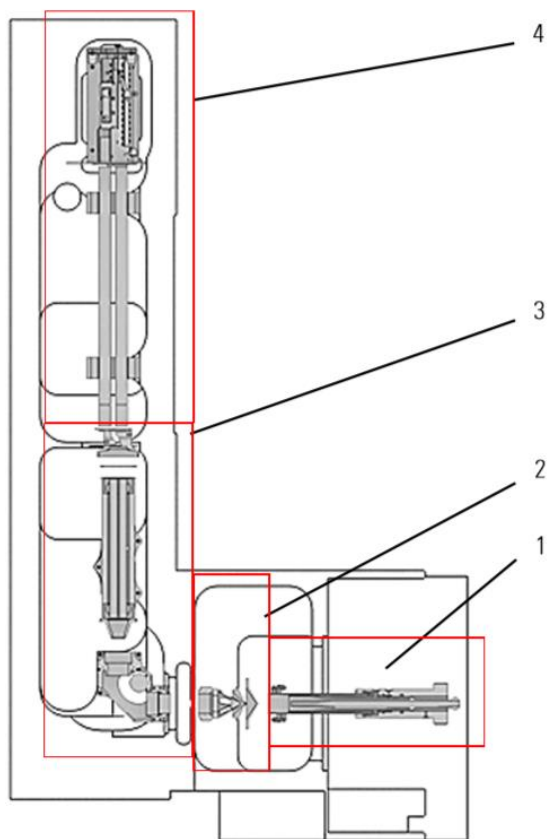


Figure 13. Thermo iCAP-Q instrumental schematic¹⁸¹

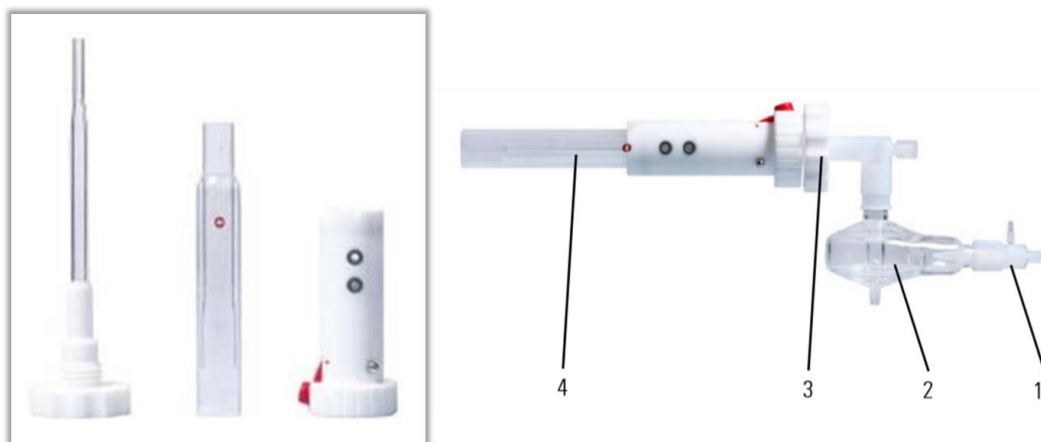


Figure 14. Right: the nebulizer (1), spray chamber (2), injector (3), and torch (4). Left: the torch and injector separately¹⁸¹.

Next, the interface, where ions generated in the plasma are transferred from atmospheric pressure to the vacuum region, is comprised of the sample cone, the skimmer cone, and the extraction lens. These are all placed in the “interface block”, shown in Figure 15, which is mounted to the plasma door for ease of access. Due to the intense heat of the plasma, the interface is water-cooled. The sample cone is made of nickel/copper, and the skimmer cone is made of nickel – platinum-tipped cones are available for this machine if needed for analysis of organics or reactive acids, like HF. The purpose of the extraction lens is to focus and accelerate the ions from the back of the skimmer cone to the intermediate vacuum region of the ICPMS.

The ion optics of the iCAP-Q include the right-angle positive ion deflection (RAPID) lens, the collision cell (QCell), and the (differential aperture) DA assembly. The RAPID lens can be seen in Figure 13, and it is used to deflect analyte ions by 90° after extraction from the interface region, which ensures that neutral particles (from the plasma) pass directly by the lens without interaction and improves reliability and reduces maintenance. After the ions are deflected, they are focused into the QCell, a quadrupole with flat rods which can be pressurized with helium (or other gas mixtures) to remove undesirable molecule ions by chemical reactions or kinetic energy discrimination. After the QCell, the ion beam is focused on the DA plate, which separates the intermediate vacuum stage from the high-vacuum analyzer region, and subsequently, the beam is deflected by the DA lens to remove residual gas particles from the ion beam.

Lastly, the ions are driven into the quadrupole mass analyzer (described in section 3.2.4.1), separating the ions by their m/z through manipulation of the radio-frequency voltage and the DC voltage applied to the rods of the quadrupole. After the selected ions exit the quadrupole, they are transferred to the dual-mode secondary electron multiplier for detection and quantification.

The exact operating settings of the iCAP-Q for this PhD work are provided in section 4.3.2.



Figure 15. Right: the interface block (1) and the plasma door (2). Left: a view of the extraction lens, located behind the cones (side not shown on the right)¹⁸¹.

3.2.4.3 Thermo Software Qtegra¹⁸²

The software provided by Thermo to operate the iCAP-Q is called Qtegra, and it is a configurable software package for elemental analyses, an “end-to-end” solution from instrumental configuration and control to experimental analyses (including calibration and isotopic quantification). The experiments can be configured to exact specifications, including the elements and isotopes of interest, dwell time at each m/z , resolution, internal standards and external calibrations, and more. Additionally, performance reports (daily checks for operational stability and sensitivity checks), autotune procedures (recalibration of specified parameters, such as torch position, gas flow, to ensure the performance reports pass), detector setup (performed when the instrumental sensitivity declines, or about once a month, which involves increasing the voltage of the detector for optimal pulse detection and performing a cross-calibration), and mass calibration (when peak widths fail the performance requirements or are not aligned correctly) can easily be performed through the software “wizards”.

The evaluation method “eQuant” available within Qtegra is employed for routine analysis of liquid samples, using external calibration to quantify concentrations of elements in an unknown sample. Calibration graphs are generated and can be customized (i.e. when one calibration standard is visibly incorrect, it can be removed from the calibration curve), and if necessary, a different evaluation strategy can be performed for each analyte or isotope of an analyte. An internal standard can be defined and utilized in this type of lab book within Qtegra, thus providing an ability to compensate for matrix effects between samples and calibration solutions. Other settings, such as quality control, can be defined and used in these lab books, however, they were not used for any of the analyses performed for this PhD project. For offline ICPMS analyses, the results are displayed as intensities (counts) and/or final concentrations (when using external calibration within the software), but for online HPIC-ICPMS analyses, the results are displayed as peak areas counts (peak heights can also be used but were not for this work).

For all of the online HPIC-ICPMS analyses, a tQuant evaluation was used within Qtegra, which is for chromatographic evaluations or “applications which require the recording and subsequent integration of transient signals”. When designing the lab book, the analytes (isotopes), dwell time, sample list (including standards), and peak detection (including peak smoothing methods) settings are defined before analysis. The dwell time should be selected to optimize the signal-to-noise ratio, as too long of a dwell time will reduce the possibility of acquiring enough data points for the correct interpolation of the peak (7–9 points per peak is normally sufficient to define the peak shape correctly). Figure 16 illustrates the effect of increasing dwell time on a peak (a neodymium standard was injected and analyzed several times to generate this data). A dwell time of ~0.01–0.001 s was typically used in the work performed for this PhD project. Calibration of this transient data can be performed within Qtegra similarly to the offline ICPMS eQuant procedure, however,

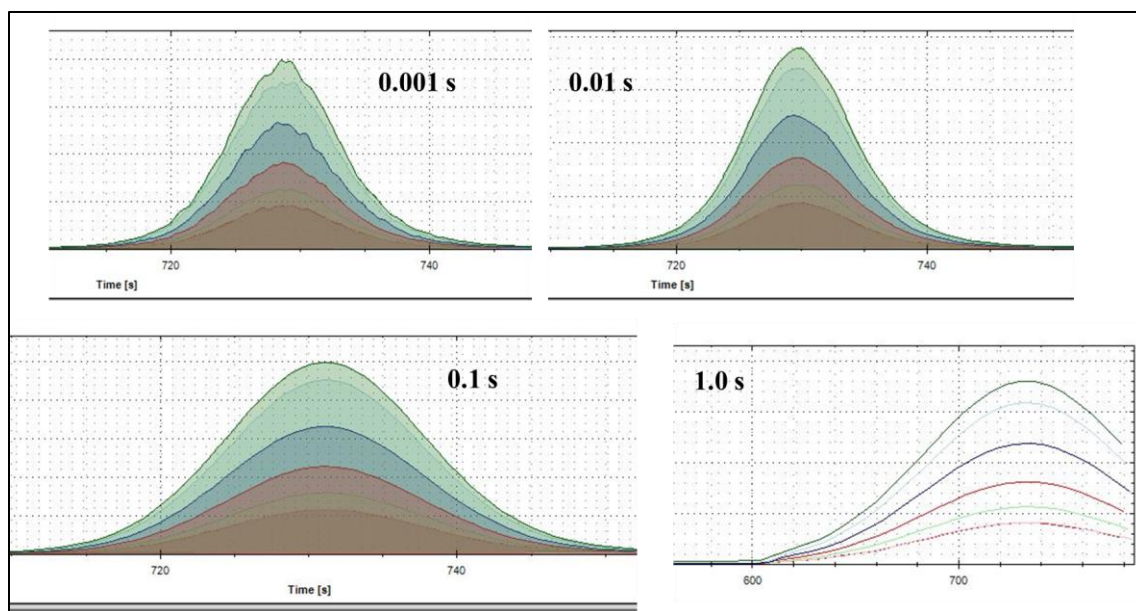


Figure 16. Effect of dwell time on a neodymium peak using the RAPID protocol.

for this project, the standards and samples were evaluated in Excel by hand using the resulting peak areas from Qtegra. After the samples have been injected, separated by HPIC, and analyzed by the ICPMS, the isotopic elution times for each isotope selected for analysis can be specified (using the final chromatograms to evaluate these times). Once the elution time and window (i.e. an elution time of 180 s with a window of 20 s looks for peaks with 160–200 s) are specified, the peak areas are integrated/calculated within the software (including accounting for the peak baseline) and provided for each isotope in each sample.

In order to operate the HPIC, Qtegra is used in tandem with another software, Chromeleon¹⁸³, which allows for communication and monitoring of the HPIC column. Within Qtegra, the Chromeleon software patch allows for specification of the elution profile and control of the pumps with the HPIC.

3.2.5 ICPMS Instrumental Mass Bias

A well-known issue of ICPMS is the instrumental mass bias that occurs due to several processes in the sample introduction system; it is a very complex problem to characterize, even though it has been thoroughly studied. There are two general types of mass bias, elemental and quadrupolar. Elemental bias occurs within the plasma since ionization energy is constant for each element (does not vary as a function of isotope), and thus any biases created in the plasma will be consistent for each isotope of that element. Quadrupolar bias occurs after ionization, where each m/z traverses the path from ionization to detection slightly differently depending on variables such as the composition of the sample and sensitivity/response of the detector for each mass (i.e. the quadrupolar mass response curve). As mentioned in various publications^{6,184–186}, processes causing bias include (see Figure 17 for a diagram of the plasma introduction system):

- 1) Mass dependent fractionation:
 - a. Sample matrix – different masses of elements in the matrix affect the way the sample is introduced into the plasma (i.e. heavier elements such as iron will be ionized preferentially compared to the lighter elements in the solution)
 - b. Instability in the plasma itself – as the ICPMS is operated, temporal shifts occur, which can be observed by repeating measurements of certified standards through the day
 - c. Plasma operating conditions – sample gas flow rates, torch position, and torch alignment all cause minor mass bias as the plasma is introduced to the mass spectrometer

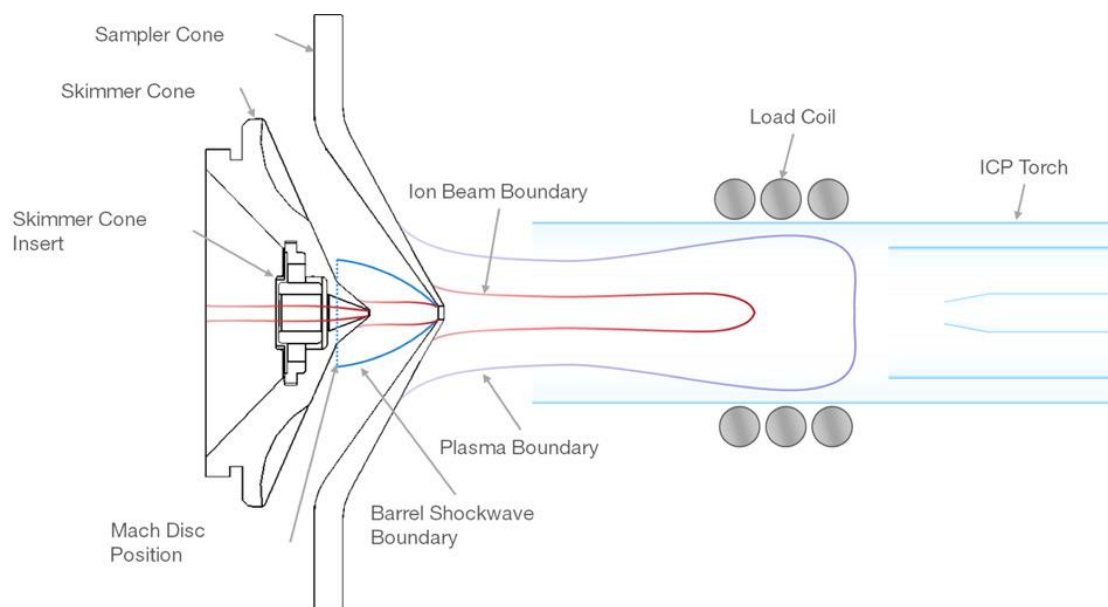


Figure 17. ICPMS interface diagram¹⁸⁷

- a. Vacuum effects – as the plasma travels through the sample cone into vacuum, it undergoes a supersonic expansion, which affects the lighter ions differently than the heavier ions, causing deflection of the lighter ions out of the main beam axis
 - b. Space charge effects – after the skimmer cone, a second expansion occurs, which further depletes the lighter ions from the sample beam via broadening of the beam by Coulombic repulsion of charges
- 2) Mass independent fractionation – it has been hypothesized that nuclear characteristics cause mass bias between isotopes of the same element, such as nuclear field shift and nuclear spin effect

There have been many efforts at creating correction correlations for each of these subsets of mass bias^{188–190}, but the method used for this work was straight-forward: measure a naturally-abundant standard for the element(s) of analysis and observe the difference between the known isotopic distribution and the measured distribution. Once this difference is measured, the deviation from

natural is calculated as a function of isotopic ratio (e.g. for neodymium, the ratios used are 142/144, 143/144, 145/144, and so forth); generally, the deviation from natural is linear as the masses increase. Figure 18 illustrates this trend for a neodymium standard measured with the RAPID system. To clarify, a $\Delta m = -2$ correlates with the ratio 142/144, and a $\Delta m = +2$ subsequently correlates with the ratio 146/144. This measurement needs to be performed every day that this element is measured due to the daily fluctuations of the ICPMS. Additionally, it will vary from instrument to instrument, so measurements of standards are a necessity in ICPMS analysis. Once this deviation from natural (i.e. mass bias) is quantified, it is used to correct the measured ratios in the sample by dividing the appropriate ratio by its corresponding mass bias factor ($R_{\text{measured}}/R_{\text{true}}$) from the mass bias measurement.

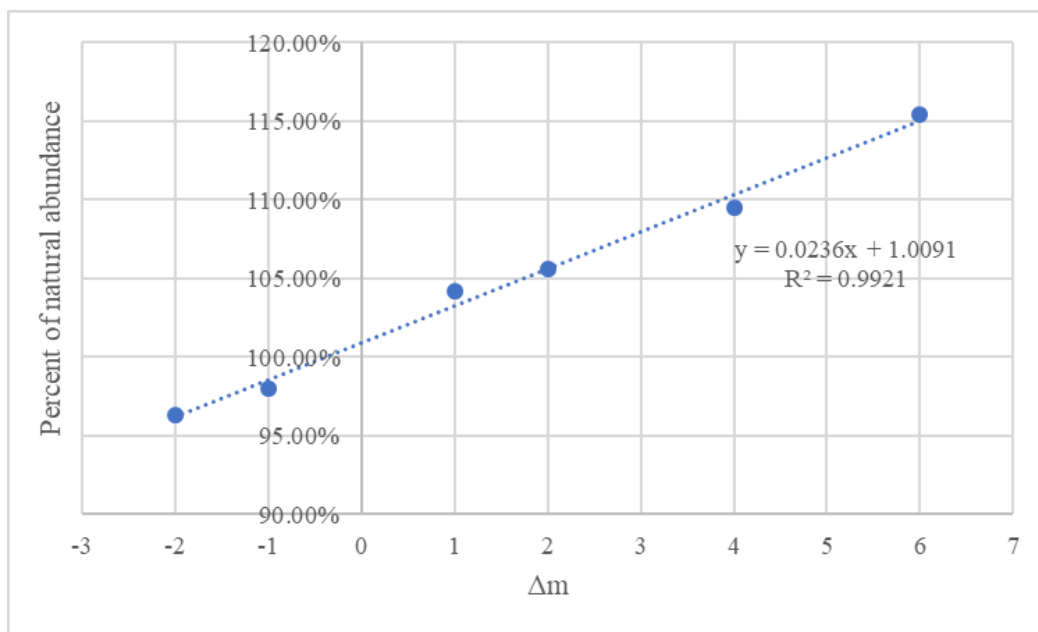


Figure 18. An example of the mass bias trend in a neodymium standard, measured with the RAPID system, where Δm is the difference in mass from 144 as a ratio (142/144 to 150/144).

3.2.6 Isotope Dilution Mass Spectrometry

3.2.6.1 General Theory¹⁹¹

Isotope dilution analysis is a well-known analytical technique based on measurements of isotopic ratios in a sample after its isotopic composition is altered by the addition of a known (measured/calculated) amount of an isotopically enriched spike. To do this analysis on an element, it must have at least two stable (or long-lived) isotopes measurable in a mass spectrometer free of spectral interferences. Figure 19 illustrates the concept of spiking one isotope in a sample (isotope b) to create a mixture of isotopes a and b, which is dependent on the isotopic ratio in the sample and the spike. To calculate the final concentration of the element in a sample, the isotopic ratios in the sample and spike are expressed mathematically (as a function of moles/atoms, mass, and isotopic abundances) and re-arranged. The derivation of the isotope dilution equation is shown in this section, assuming only two isotopes in the element.

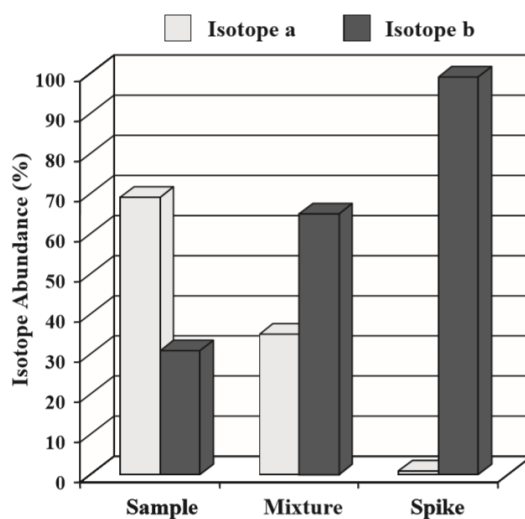


Figure 19. Illustration of the isotope dilution principle for an element containing two different isotopes, a and b¹⁹¹.

The mass (where N is atoms) of each isotope in the mixture can be presented as a sum of the sample (S) and spike (sp) isotopic masses:

$$N_m^a = N_S^a + N_{sp}^a \quad (3)$$

$$N_m^b = N_S^b + N_{sp}^b \quad (4)$$

From these equations, the ratio of a/b in the mixture can be defined as, where A is the isotopic abundance of the isotope in its solution (in atom percent, for sample or spike):

$$R_m = \frac{N_m^a}{N_m^b} = \frac{N_S^a + N_{sp}^a}{N_S^b + N_{sp}^b} = \frac{N_S A_S^a + N_{sp} A_{sp}^a}{N_S A_S^b + N_{sp} A_{sp}^b} \quad (5)$$

Rearranging this equation to solve for the mass of the sample (N_S) in atoms gives:

$$N_S = N_{sp} * \frac{R_m A_{sp}^b - A_{sp}^a}{A_S^a - R_m A_S^b} \quad (6)$$

This equation is the most basic “isotope dilution equation” used in IDMS. However, using the isotopic ratios of a/b in both the sample (R_S) and the spike (R_{sp}), which are measured with an ICPMS, a new equation can be written:

$$N_S = N_{sp} * \frac{A_{sp}^b (R_{sp} - R_m)}{A_S^b (R_m - R_S)} \quad (7)$$

Since the spike is measured in terms of weight, it may be more convenient to convert the atoms in this equation to elemental mass in each solution (m_x, where x is the sample/spike) using molar mass (a_x) and Avogadro’s number (N_A):

$$N_x = m_x * \frac{N_A}{a_x} \quad (8)$$

$$m_S = m_{sp} * \frac{a_S A_{sp}^b (R_{sp} - R_m)}{a_{sp} A_S^b (R_m - R_S)} \quad (9)$$

The exact molar mass of the spike and sample can be measured by the ICPMS using the atom percent (AP_x) and the isotopic mass (M_x , grams/mol):

$$a_x = AP_x^a * M^a + AP_x^b * M^b \quad (10)$$

Lastly, to directly calculate the elemental concentration in the sample, the correlation of elemental mass and weight to concentration ($m_x = C_x * W_x$) changes the “isotope dilution equation” to:

$$C_S = \frac{m_{sp}}{W_S} * \frac{a_S A_{sp}^b (R_{sp} - R_m)}{a_{sp} A_S^b (R_m - R_S)} \quad (11)$$

Where all these variables are directly measured (weight of the sample, mass of the spike) or measured with the ICPMS (molar mass of the sample and the isotopic ratios).

Compared to other calibration strategies (external calibration, standard addition), there is no parameter regarding instrumental sensitivity (as can be seen with the above derivation). This provides an advantage because any variation due to instrumental instabilities (signal drift or matrix effects) will not influence the final value for the elemental concentration in the sample.

The uncertainty of the concentration will depend solely on the uncertainty in the measurement of the isotopic ratios since the elemental atomic weights are known and the mass taken from both the sample and spike can be gravimetrically determined. Generally, if the sample is known to be of natural composition, R_S is known, and R_{sp} can be obtained from a certificate (if a certified tracer or spike). When this is the case, the only parameter experimentally determined is R_m , and it can be performed with high accuracy and precision with an ICPMS.

Another advantage of IDMS is that, once the sample is spiked and isotopic equilibration is achieved, any possible loss of the mixture will not influence the final result because any aliquot of the isotope-diluted sample will have the same R_m . For the same reason, at this point, no dilution factor is necessary for any concentration calculations, unlike other analytical methods

and calibration techniques. Before diluting with the spike, however, it is necessary to take into account any dilution factors or loss of solution (either spike or sample) that can contribute to the error of the overall measurement.

Due to these advantages, IDMS is regarded as a reference technique or highly qualified primary analytical method. Since the concentration is directly tied to the measurement of R_m , no external instrumental calibration or standard addition is needed, which is another advantage in terms of total time for analysis (compared to other analytical procedures).

Other factors to consider during IDMS: the enriched isotope should behave identically to the natural element throughout the entire procedure, there cannot be any spectral interferences on either isotope, mass bias and detector dead time must be monitored and corrected for, and blank measurements are imperative (any contamination affecting the diluted sample will bias the R_m values). If any of these are not taken into account, the expected accuracy of R_m and the corresponding concentration will not be obtained.

Two modes of spiking can be performed with IDMS depending when the spike is added to the sample, called “species-unspecific” and “species-specific” spiking modes. In the “species-unspecific” mode, the spike is added after complete separation of the naturally occurring species in the sample has occurred (i.e. post-column spiking), and the spike may exist in a different chemical form than the species being analyzed. This is useful when the structure/composition of the species of interest is not exactly known or the isotopically enriched compounds are not commercially available or cannot be synthesized in the same species. However, this mode does not offer all the typical IDMS advantages mentioned earlier, and final isotopic ratio varies across the transient signal which requires an integration of the “isotope ratio chromatogram”. In the “species-specific” mode, the species of both the spike and sample match, the spike is added at

the beginning of the analytical procedure (i.e. pre-column spiking), and the composition/structure of the species must be known. In this mode, the isotope ratio stays constant across the whole peak as the element is eluted from the column, and all the IDMS advantages are exploited. This is the mode utilized for all IDMS experiments conducted within this PhD work.

3.2.6.2 Parameters Affecting Isotopic Ratios¹⁹¹

Obtaining accurate and precise analytical results involving trace element analysis requires accurate and precise isotopic ratios from transient signals, and unfortunately, most mass spectrometers suffer from several limitations. These limitations include spectral interferences, detector dead time, and mass discrimination. Other parameters that affect the instrumental precision of isotopic ratios include the statistics of ion counting and random error propagation in IDMS analysis.

IDMS can only be performed accurately if the two isotopes in question are free of spectral interferences, and depending on the instrument, various measures can be taken to ensure this. For ICPMS, options include collision/dynamic reaction cells or chromatographic separation, followed by mathematic corrections as a last resort. The reaction cell is pressurized with an appropriately selected gas (NH_3 , CH_4 , or CO are most commonly used in a dynamic reaction cell) to produce collisions and reactions between the ions from the plasma and the gas molecules, and this process eliminates (or at least reduces) the interfering ions without affecting the analyte ions. Chromatographic separation (as discussed in this dissertation) eliminates the majority of isobaric and polyatomic interferences, as the interference is eluted off of the column at a different time than the isotopes of interest. If there are any additional spectral interferences that cannot be eliminated with either of those techniques (such as hydrides), those masses must be monitored, and mathematic corrections performed to correct the isotopic ratios.

Detector dead time is problematic at high counting rates for ICPMS ($\sim 10^6$ counts per second), and the number of counts registered will not match the number of counts that actually occur, which is an issue when extreme isotope ratios need to be measured. To obtain good counting statistics, the intensity of ions with low abundance need to be increased, and that drives up the count rate of the other ions, causing the high abundance isotopes to be affected by dead time issues. There are corrections for dead time that can be manually performed, however, dilutions can be performed to optimize the count rates (and keep under 10^6 cps). The effect of detector dead time on transient signals is the observation of varying isotopic ratios during peak elution due to irregular peak shape – the top of the peak may be more affected than the front or tail of the peak (where there are fewer counts). The Qtegra software indicates when the detector changes modes (to analog mode) due to high count rates, and a dilution can be performed to acquire more optimal count rates.

As described in section 3.2.5, the effect called mass bias (or discrimination) is well known, causing heavier isotopes to be transmitted through the ICPMS more efficiently than lighter isotopes. The consequence of this on IDMS is that R_m is always biased towards the heavier isotopes and needs to be corrected. It can be corrected following the procedure described in section 3.2.5, where a natural standard (with a consistent isotopic composition of the same or a neighboring element) is measured throughout the day of the sample analysis, and the mass bias factors obtained from that are used to correct the sample ratios.

Precision is dependent on the MS instrument selected for analysis (e.g. an MC-ICPMS can achieve a relative standard deviation a magnitude or two lower than a quadrupole ICPMS), however, in cases where ion counting is used (quadrupole ICPMS), precision is limited by the statistics of the ion counting system. This is proportional to the square root of total counts measured, which correlates a high counting rate to a high precision (low standard deviation). For the measurements

using a constant sample intake (offline ICPMS), ion count rate can be improved through an increased integration time (i.e. dwell time) and/or the number of scans along the mass spectrum. For transient online ICPMS measurements, a trade-off must be made between the integration time and the correlating peak shape (described and illustrated in section 3.2.4.3) for optimal precision. If too many isotopes are being monitored within the ICPMS, causing too slow mass spectral scanning, then an effect referred to as “spectral skew” may occur, which produces an inconsistent ratio as a function of the transient signal over the course of the peak. This is problematic when the ratio is assessed at each point on the peak as it is eluted off the column, however, using peak integration (peaks in the chromatogram are integrated, obtaining a baseline-subtracted peak integral area, which are used to calculate the necessary ratios), the spectral skew effects are minimized. The compromise with this approach is a degradation of precision due to the loss of the precision inherent in rapid sampling of the isotopic pair during measurement. When considering precision of the ratios during IDMS measurements with a transient signal (HPLC-ICPMS), a trade-off must occur between potential spectral skew and counting statistics (peak integration).

Lastly, the uncertainty in the calculated concentration obtained through IDMS is a function of the measured isotope ratio and its uncertainty in the mixture (R_m), assuming the other sources of error are negligible. Using an approximate numerical method of differentiation to calculate uncertainty, starting with the final “isotope dilution equation” derived in section 3.2.5.1, and taking its derivative:

$$\left(\frac{\delta C_S}{C_S}\right) = \left[\frac{R_m(R_S - R_{Sp})}{(R_m - R_S)(R_{Sp} - R_{Sp})} \right] * \left(\frac{\sigma R_m}{R_m}\right) \quad (12)$$

The term in brackets is referred to as the “error magnification factor” and depends on all three ratios, however, only one (R_m) can be optimized. This factor becomes large as R_m approaches

either R_s or R_{sp} increasing the uncertainty of the measurement – when R_m approaches R_{sp} , it is termed “over-spiking” and when it approaches R_s , it is “under-spiking”. The overall effect of this factor is dependent on the ICPMS precision and the sample/spike compositions, however, mathematically, the ideal R_m occurs at $\sqrt{R_s R_{sp}}$. This is visualized in Figure 20, where nominal ratios were chosen ($R_s = 25$, $R_{sp} = 0.01$) to calculate the error magnification factor – it can be seen that the lowest point occurs at an $R_m \sim 0.05$, corresponding with the theoretically optimized R_m . The effects of over- and under-spiking can also be observed as a large increase from the optimal R_m , correlating to an increase in the uncertainty of the concentration measurement. In practice, the best precision is achieved for an R_m of one, where the spike isotope (b) and main sample isotope (a) are at a near identical concentration.

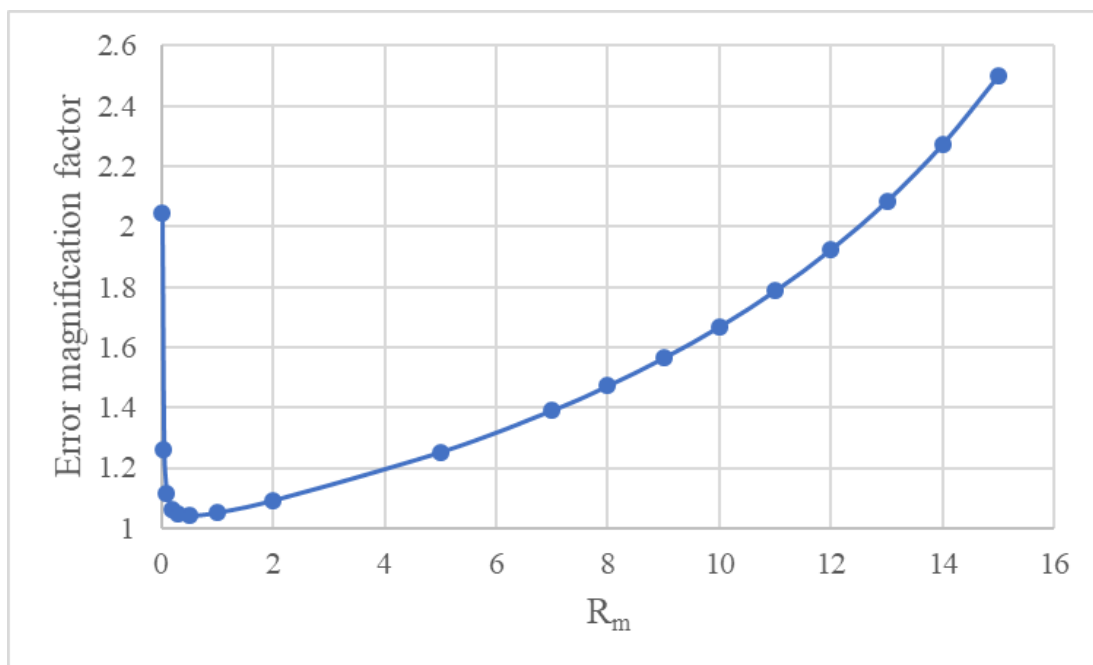


Figure 20. A calculated error magnification curve for an R_s of 25 and R_{sp} of 0.01, showing an optimal R_m at 0.05.

3.2.5.3 General IDMS Procedure for RAPID

The steps for an IDMS analysis generally are as follows:

- 1) Using weighted dilutions, create a spike at the same level of concentration as expected in the sample
- 2) Spike the sample at close to a 1:1 ratio
- 3) Dilute/dissolve then analyze spiked, unspiked, and the spike mixture itself
- 4) Correct isotopics for mass bias from natural standard
- 5) Plug the corrected isotopic distributions, weights (spike/sample), as well as concentration of spike into a worksheet which uses the equations from section 3.2.5.1 to determine an elemental concentration in the sample
- 6) Repeat for each element that was spiked

Every IDMS measurement performed for this PhD work had a sample list of:

- HNO₃ blank
- Natural standard (10/20 ppb) for mass bias correction
- Matrix blank
- 4–5x replicates of the sample
- HNO₃ blank
- 4–5x replicates of the spike + sample
- HNO₃ blank
- 4–5x replicates of the spike
- HNO₃ blank
- Natural standard (10/20 ppb) for mass bias correction

Additional standards for mass bias correction were injected as necessary between sets of sample/spike injections for samples with more complex matrices and/or longer sample sets to ensure no change in mass bias occurred over the course of the experiment.

To calculate the uncertainty of the final elemental concentration using this method, multiple terms were summed: the instrumental precision (deviation over the 4–5 replicates) of all three ratios, the uncertainty of the weights (*measured number in grams*/0.002 g for both sample and spike), and the mass bias corrections (using the precision/standard deviation of the measured standard replicates).

3.3 Radiation Detection Principles

Semiconductor radiation detectors operate based on the interaction of gamma-rays with the electrons in the material by photoelectric absorption, where an electron absorbs the entirety of the gamma-ray energy and subsequently loses that energy through coulomb interactions with other electrons. This process creates electron-hole pairs (each electron given enough energy will leave a corresponding hole in the lattice of the material) that migrate through the material given an applied electric field. The characteristics of both the electron and hole mobilities are dictated by the material properties of the semiconductor, such as bandgap width, and atomic number. Ideally, to fully characterize the incident gamma radiation, 100% of these charge carriers should be collected by the detector electrode; unfortunately, recombination of the electron-hole pair may occur, causing annihilation. Impurities in the material (e.g. metallic atoms occupying lattice positions) are the main cause of recombination, as they can act as recombination centers, trapping both electrons and holes within the impurity and forcing annihilation or loss of charge collection during data acquisition. Secondly, structural defects in the crystal lattice can also contribute to this

charge trapping phenomenon and charge carrier losses¹⁹². Thus, purity of the semiconductor material is an important characteristic driving good radiation detection within the detector.

Both high-purity germanium (HPGe) and cadmium zinc telluride (CZT) detectors are semiconductors; however, HPGe detectors are the dominant semiconductor detector currently used for most nuclear applications due to its high energy resolution. Techniques for producing HPGe began in the 1970's, and to this day, large crystals of highly-purified germanium are produced to provide a high-resolution radiation detection capability. Its bandgap energy at room temperature is too small for good detection (thermally-induced leakage would occur), so HPGe detectors must be operated at low temperatures (77 K) using either liquid nitrogen or an electro-mechanical cooler. Additionally, due to its low atomic weight, its overall photopeak efficiency (fraction of events captured under the full-energy peak) is fairly low (<6%)¹⁹³.

Radiation sensors operated with CZT crystals are a newer technology than HPGe detectors¹⁹⁴, and research is still being performed on the material to further optimize and develop it as an advanced technology. However, current detectors are available as commercial off-the-shelf systems and have a niche to fill between the resolution of an HPGe and the efficiency of a sodium iodide scintillation detector. The main issues with CZT crystals are the ability to grow them in large sizes (>1 cm) and their impurity content, which causes incomplete charge collection (via hole trapping) and subsequently produces deviations from the typical Gaussian peak shape seen in gamma spectra. This deviation from Gaussian is created by the low-energy tail (shown in Figure 21), which is prominent in all CZT spectra and for quantitative analysis must be compensated for by various peak fitting algorithms¹⁹⁵. Conversely, the gains from using a CZT (compared to an HPGe) are higher photopeak efficiency and the ability to operate at room temperature. Table 5 lists the main material and detector characteristics for both an HPGe detector and a CZT detector.

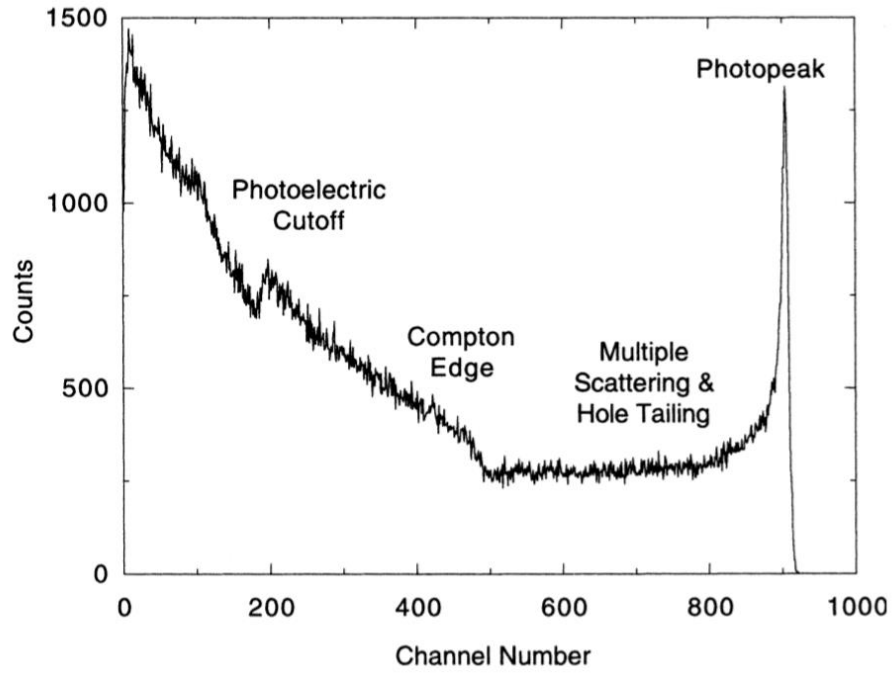


Figure 21. Simulated pulse height spectrum for a CZT detector from incident radiation with an energy of 300 keV by Toney¹⁹⁶ et al.

Table 5. Comparison of material/detector characteristics between HPGe and CZT^{192,193}.

Characteristic	HPGe	CZT
Atomic number (Z)	32	30/48/52
Bandgap (eV)	0.72	1.64
Ionization energy (eV per e-h pair)	2.98	5.0
Photopeak efficiency @ 662 keV	~1.5%	~7.0%
Energy resolution @ 662 keV (FWHM)	900 eV	11.6 keV

A CZT detector was selected for this study due its small form factor, high resolution (compared to a sodium iodide detector), and ability to operate at room temperature (unlike an HPGe).

3.3.1 Solid Angle Concept

When calculating efficiency of a radiation detector, the solid angle between the radioactive source and the detector must be considered. Since radiation sources emit radiation isotropically, the angle between the source and the detector determines the fraction of the emissions that will interact with the detector. Figure 22 illustrates this concept with a simple case: a point source a distance d from the detector of radius a . This concept is important to remember when optimizing the response of a detector from a source in various geometries. The more interactions between the detector and radiation emitted from the source, the more accurate the resulting spectrum will be.

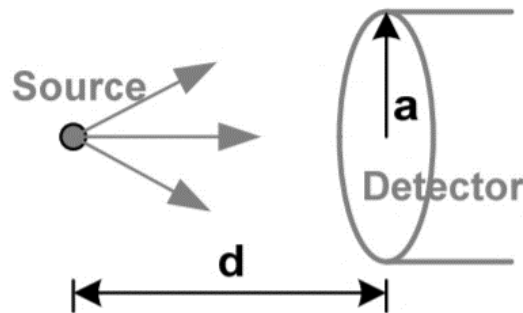


Figure 22. Illustration of the source-detector relationship for a solid angle calculation.

3.4 Uncertainty Calculations

For this project, the main contributors to the overall measurement uncertainty are instrumental precision, uncertainty of the standards used for calibration, error of the balance (if weights are used), and error of the pipets. However, the contribution from instrumental precision is at least a magnitude larger than the other contributors, so they become negligible when uncertainty is calculated. This precision is calculated as a relative root-mean-square deviation, which is essentially the standard deviation of the replicates of a measurement (generally samples are measured in triplicate). Once this relative standard deviation $(\Delta x)/x$ is calculated, it was propagated through the rest of the calculations accordingly (also as a function of squared errors), following this general function:

$$C = aA + bB \quad (13)$$

$$\sigma_C = \sqrt{(a^2 \sigma_A^2 + b^2 \sigma_B^2)} \quad (14)$$

CHAPTER 4: EXPERIMENTAL

4.1 Instrumentation and NACIL Capabilities

The NACIL group at ORNL can handle a wide range of radioactive sample types, using facilities ranging from labs within the Radiochemical Engineering Development Center (REDC) working with curie-levels of radioactivity to various cleanroom spaces in the Ultra-trace Forensics Science Facility. Radiological containment resources include hot cells, gloveboxes, and C-zoned fume hoods.

NACIL also contains the Neutron Activation Analysis (NAA) laboratory at ORNL, located in the High Flux Isotope Reactor (HFIR) facility. The HFIR is the highest, reactor-based flux neutron source for research in the United States, operating at a consistent 85 MW¹⁹⁷. NACIL's NAA laboratory is an irradiation facility that can, on average, obtain a flux $\sim 10^{14}$ n cm⁻² s⁻¹ of thermal neutrons. Its capabilities include a remote-handling cubicle to receive samples post-irradiation, as well as a decay station within the HFIR pool if the samples need to cool before receipt in the lab. The computational model utilized for this research accurately reproduces the flux spectrum within the exact pneumatic tube used for irradiation, thus enabling accurate prediction of total fissions in each sample.

Specifically, the instrumentation for this work includes: a Thermo Scientific™ Dionex™ ICS-5000+ HPIC system directly coupled to a Thermo Scientific iCAP™ Q quadrupole ICPMS (shown in Figure 23). The HPIC system includes an AS-AP autosampler, a gradient mixing pump capable of combining four different eluents in a programmable gradient, and a thermal compartment containing the injection loop and separation column, able to maintain temperatures 5–85°C for

constant elution times and reproducibility. For this work, these thermal compartment options were not utilized, instead a constant temperature of 25°C was implemented.

The ICPMS is equipped with: a wide-range sensitivity detector (from mg/L to pg/L), a robust torch capable of withstanding the introduction of various salts and organic matter from the HPIC eluents, and a wide bore (high salt) nebulizer which can nebulize solutions of higher density and organic content. All data were processed using the Thermo Fisher Scientific Qtegra software. Operating parameters are provided in the first publication from this work¹⁹⁸.

In 2019, additions were made to this method, including an inline Mirion™ co-planar grid CZT gamma detector and a Thermo Scientific Dionex UFC-3000 automatic fraction collector (see Figure 24). Shown in Figure 25, a custom-designed, 3D-printed shield (filled with steel shot), produced by the ORNL Radiation Detection and Imaging Group, contains the CZT detector in the hood to lower the gamma background which exists in the lab, caused by the large number of radioactive samples received and stored there for NACIL analysis. A sample loop was made to encircle the detector crystal post-separation, giving it a dwell time of approximately 30 s before analysis by the ICPMS. The operating parameters of the CZT detector are provided in Table 6 using a Canberra Lynx. The fraction collector was installed to separate and collect individual samples of each element by elution time for analysis by a different instrument (either an MC-ICPMS or an HPGe detector) for a higher sensitivity analysis. It was controlled separately from the ICPMS with a standalone laptop using Chromeleon 7.2.10. Each of these additions (CZT or fraction collector) can be used or bypassed for any analyses performed with RAPID, depending on the sample and its application. Figure 26 displays a process diagram of the analytical setup.



Figure 23. Photos of the original coupled HPIC-ICPMS system in a radiological fume hood.

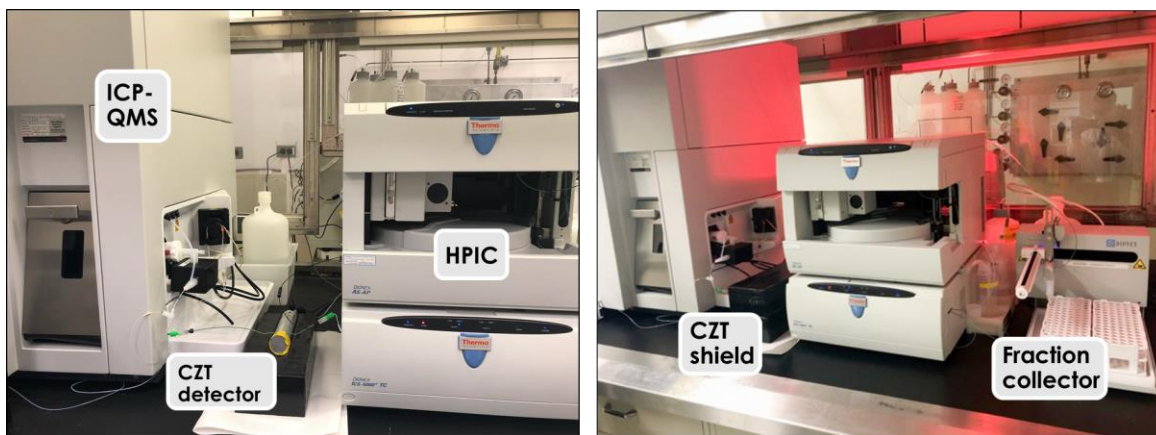


Figure 24. Updated HPIC-ICPMS system (2019), including a CZT detector and fraction collector.



Figure 25. A 3D-printed shield designed with CZT dimensions for use in fume hood (CZT and sample loop also pictured).

Table 6. CZT operating parameters within the Canberra Lynx system.

Parameter	Value
Operating voltage	-1200 V
Coarse gain	4.76
Fine gain	1
LLD mode	Automatic
Rise time	1 μ s
Flat top	0.8 μ s

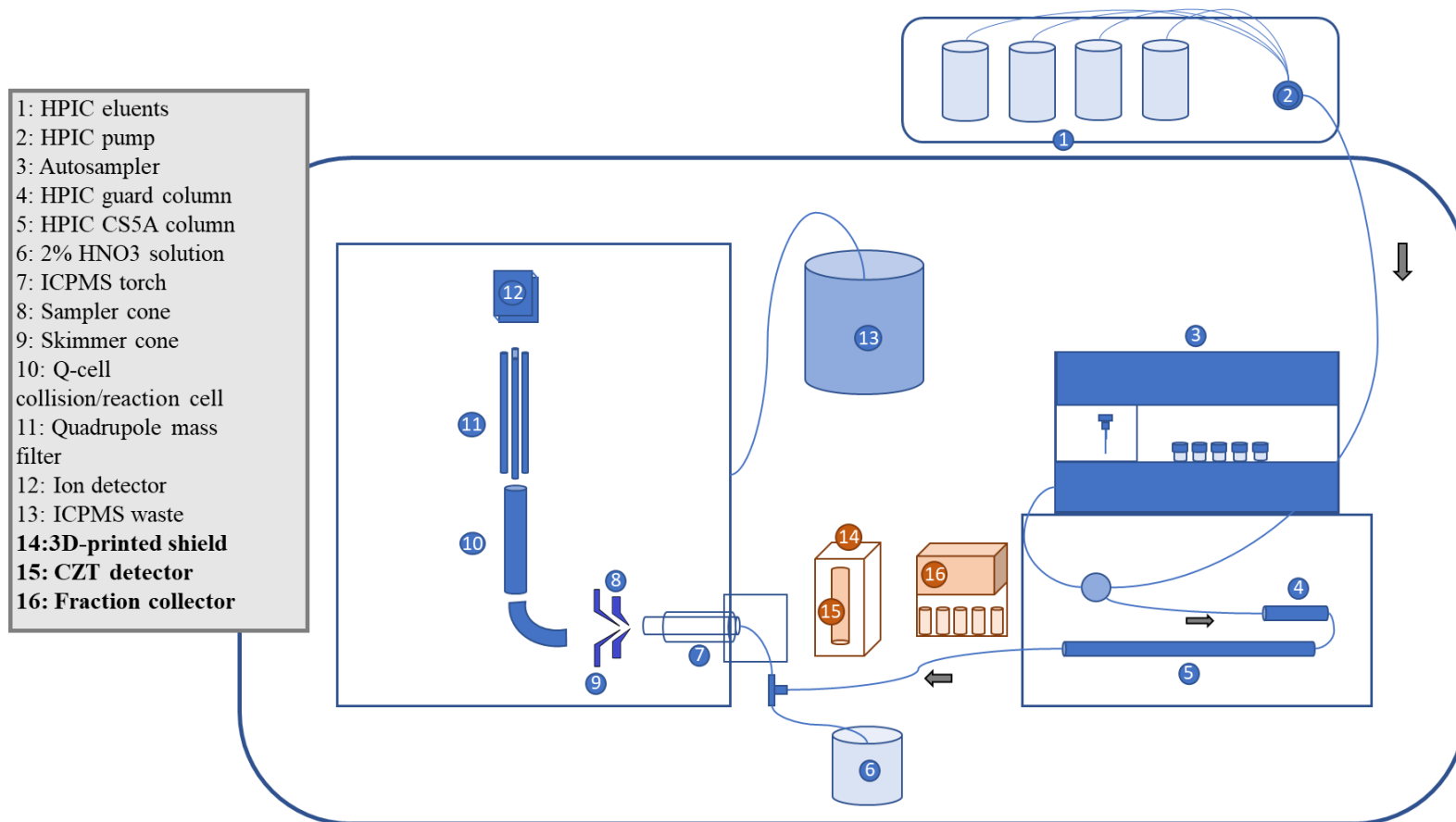


Figure 26. Process diagram of RAPID, where orange indicates a new addition to the original method. The sample line can be diverted inline to either of the orange additions 15 and 16 (or bypass both of them).

4.2 Nuclear Physics Modeling Codes

4.2.1 Fission Product Modeling

Two different software programs were utilized specifically to model fission products: decay modeling software developed at ORNL, the Oak Ridge Isotope Generation (ORIGEN) code (located within the ORNL Standardized Computer Analyses for Licensing Evaluation [SCALE] code), and the Stopping and Range of Ions in Matter (SRIM) software.

The SCALE code is a modeling and simulation suite used primarily for nuclear safety analysis and nuclear reactor design (criticality safety, reactor physics, radiation shielding, radioactive source characterization, and uncertainty/sensitivity analysis) created and maintained by ORNL¹⁹⁹. It integrates dozens of computational models and Monte Carlo radiation transport solvers and includes up-to-date nuclear libraries and processing tools for various neutronics, activation, decay, and depletion calculations. Within SCALE, ORIGEN is designed to calculate time-dependent isotopic concentrations during and after irradiation for the complete set of nuclides produced by nuclear irradiation (including neutron activation)²⁰⁰. Depletion codes usually involve coupling reactor lattice physics transport methods that solve for the neutron flux spectrum and generate the appropriate cross-sections then simulating the corresponding time-dependent isotopic evolution as radioactive decay occurs. ORIGEN does this as a depletion model coupled with a neutron transport model (to obtain problem-dependent cross-section libraries) for use in various applications. Another code built into SCALE/ORIGEN is COUPLE, where users can define specific cross-section values measured directly from a particular system (or nuclear reactor) to predict the accurate irradiation/decay from that exact system. Utilizing COUPLE and ORIGEN together

allows for a simulation of a known system and subsequent prediction of the resulting fission products, which was useful for this PhD project.

For this project, fission product inventories were predicted by ORIGEN and used to check the accuracy of results for samples irradiated in the HFIR facility post-irradiation. For his PhD work, as a previous graduate student in NACIL, Dr. Knowles fully characterized the neutron flux that the NAA samples are exposed to at the HFIR in Pneumatic-Tube 1²⁰¹ (PT-1), so an exact comparison could be made for any sample irradiated in that configuration.

In the work completed for this dissertation, for each irradiated sample, an input deck was created (in ORIGEN), specifying the parameters highlighted in Figure 27, and the expected fission product inventory was calculated, utilizing the neutron flux measured by Dr. Knowles and compiled through COUPLE. The final fission product inventory was given as a function of isotopic masses to compare with the ICPMS analysis of the target. Notably, ORIGEN also has the capability to decay these fission products, so an accurate prediction was made to each measurement at the time of analysis.

Secondly, the SRIM software calculates the stopping power and range of any ion (with any energy up to 2 GeV/atomic mass unit) into any material through quantum mechanical collision modeling and the Bethe-Bloch equation. This software is continually updated and further details can be found in their publications²⁰². The input parameters needed for this software are the ion (isotope), its energy, and the target material. For this project, SRIM was used to calculate the penetration of fission products into the target vessel during irradiation.

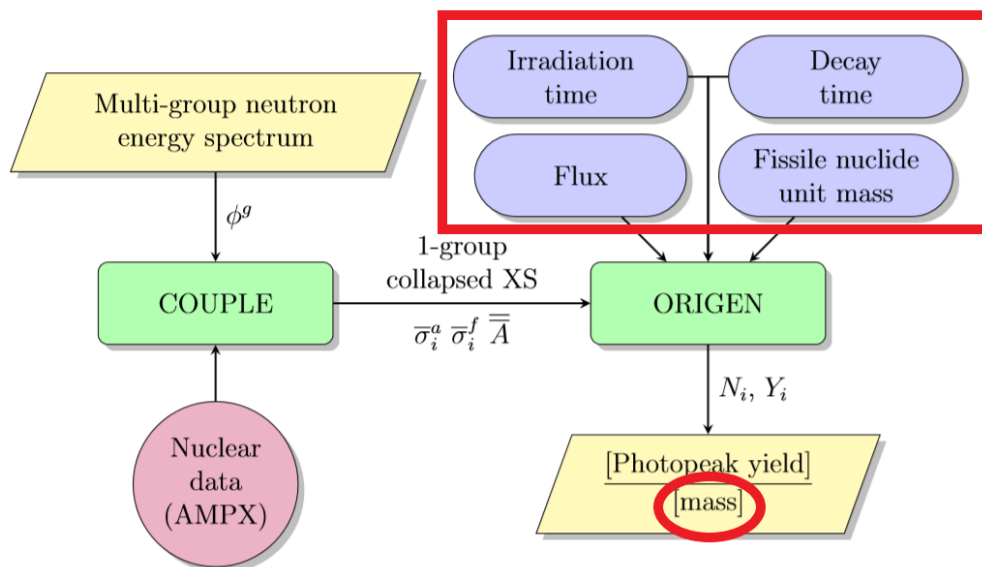


Figure 27. Flow of data for the ORIGEN models, as illustrated by J. Knowles²⁰¹. The red square highlights the user inputs for this project, and the red circle shows the subsequent data output by the model.

4.2.2 MCNP Detector Response Modeling

MCNP was used to generate gamma spectra of the expected separated chemical fractions going through the inline system. To do this, an input deck was generated using known dimensions of the CZT and its housing. The sample loop was approximated as a cylinder surrounding the housing of the detector around the CZT crystal. The final geometry can be seen in Figures 28 and 29, and an example input deck can be found in the appendix.

The source term for these models was approximated as a hollow cylinder surrounding the housing of the detector around the crystal. The source definitions for each experiment will be provided in the appropriate section.

To generate more realistic spectra, an energy broadening function for a CZT was needed. Due to the relative novelty of these detectors, data for this function was not found in any available

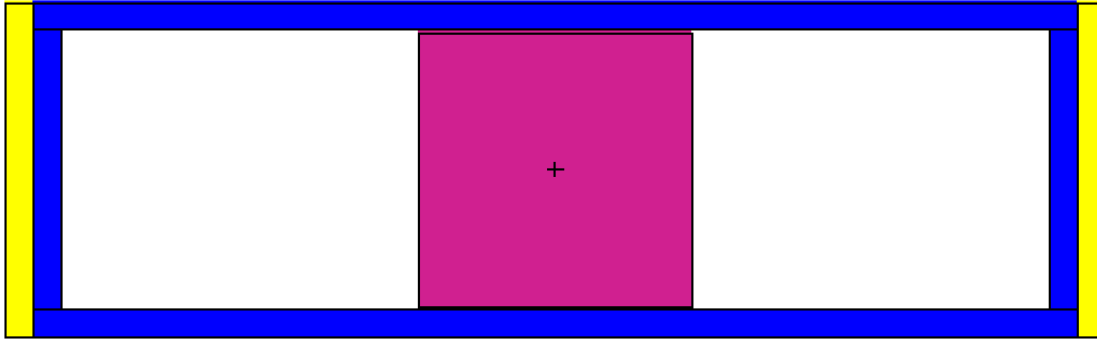


Figure 28. A side view of the CZT crystal (pink) within its aluminum housing (blue), surrounded by the cylindrical loop source (yellow).

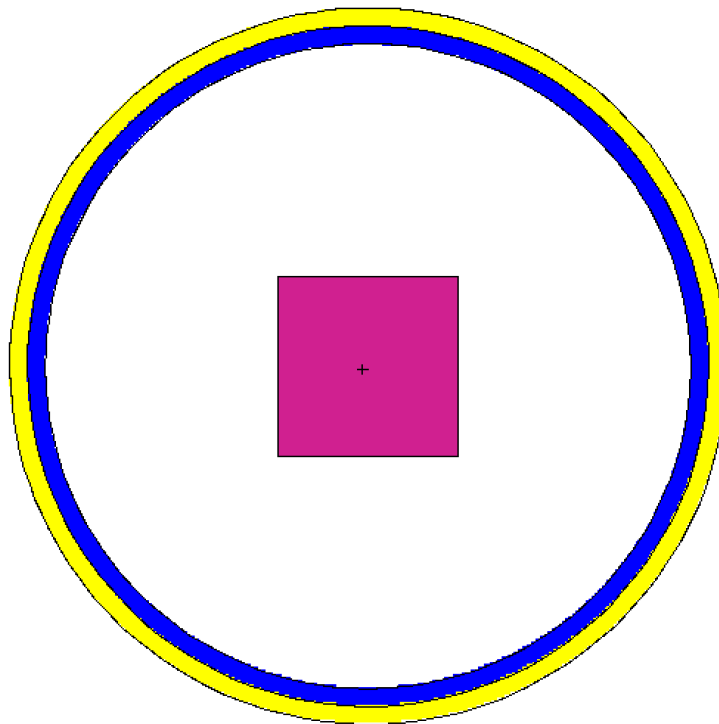


Figure 29. A top view of the CZT crystal (pink) within its aluminum housing (blue), surrounded by the cylindrical loop source (yellow).

literature; however, using the measured calibration spectrum (with $^{133}\text{Ba}/^{137}\text{Cs}$), the full width at half maximum as a function of energy was approximated for the CZT detector using a python script written by another graduate student. The peaks were fit with a combination function of an exponential low-energy tail and a Gaussian peak.

4.3 Experimental Preparation

This section will describe eluent preparation, preparation of the ICPMS for operation, and the various samples analyzed with RAPID during the developmental period and tenure of this PhD project.

Basic reagents used continuously for this work include deionized water, metals-grade nitric acid, and various elemental (e.g. natural neodymium, uranium) and isotopic (e.g. ^{150}Nd , ^{235}U) standards acquired from Inorganic Ventures. Any other reagents used specifically for an experiment will be mentioned in the associated paper or results section in this dissertation. A list of elements and which standard was used for each is given in the appendix.

4.3.1 Eluent Preparation

The four eluents used in this study are PDCA, oxalic acid, DGA, and HCl. Three of these are created from crystalline batches purified to the 99%+ trace-metals purity level, however, it was discovered that this purity was not high enough for the oxalic and DGA eluents. The next step was to recrystallize them in the lab using the following steps²⁰³:

- 1) Obtain solubility of oxalic acid in water (1 g oxalic: 1 g water @ 95°C ²⁰⁴) and DGA in water (0.7 g DGA: 1 g water @ 25°C ²⁰⁵)
- 2) Turn on Hot Block to the relative temperature for either oxalic or DGA

- 3) Weigh out the necessary ratios of the material (e.g. 50 g water and 50 g oxalic) in a Hot Block-safe container using deionized Milli-Q water
- 4) Dissolve the material in the water
- 5) Remove the container from the Hot Block and let cool to room temperature
- 6) Place the container in a refrigerator overnight
- 7) Drain the excess water and rinse with Milli-Q water
- 8) Dry the crystals with a Buchner filter

For each recrystallization, the lot numbers were noted in a laboratory notebook, which is important as some lots were observed to have higher levels of contaminants. If the levels of contamination are observed to be high after one recrystallization, then this process was repeated for a higher purity material.

It was also observed that the oxalic acid still had high levels of barium contamination (which is important when separating cesium and barium of a sample), and this procedure was changed to dissolving ~0.7 g oxalic per 1 g water at 70°C. Per a study on the purification of oxalic acid²⁰⁶, when the oxalic acid is dissolved at 100°C, there is a high probability that the purity of the crystals is lower due to the solution evaporating and subsequent increase of the concentration of impurities in the solution. Additionally, it is noted in this study that larger crystals will have fewer impurities because there is less surface area of the crystal for the impurities to adsorb onto as the solution cools and the crystals form. Larger crystals are formed if the rate of cooling after dissolution is slowed down (i.e. the container is not placed directly in the refrigerator).

Once the starting materials are adequately purified, the eluents can be created. It should be noted that the oxalic acid bought from a provider is pure oxalic acid, while the recrystallized oxalic is a dihydrate, which changes the molar mass. The concentration of each eluent is given in Table 7 as

well as the approximate pH. The buffer material used for pH balancing was ammonium hydroxide, since other hydroxides (sodium or lithium) leave salt residue on the cones of the ICPMS.

The eluents were made in 1 L bottles, and the procedure was as follows:

- 1) Leach bottle using ~4M trace-pure nitric acid
- 2) Fill bottle to ~0.9 L with Milli-Q water
- 3) Measure out the proper amount of acid as given in Table 7 and shake to dissolve
- 4) Buffer the pH to ~4.8 with ammonium hydroxide (ranging from ~10–30 mL depending how fresh the solution is)
- 5) Top off bottle to 1 L with Milli-Q water
- 6) Store in a refrigerator until use
- 7) Once brought into lab, measure barium content directly with ICPMS (no separation) – if barium content/contamination is high, then do not use for trace-level cesium/barium separations

Table 7. Eluent properties

Eluent	Molar Mass (g/mol)	Goal concentration in 1 L	Mass used in 1 L	pH
PDCA	185	6mM	1 g (+ 5.15 mL glacial acetic acid)	4.8
Oxalic acid (dihydrate)	90 (126)	150mM	12.5 (~18) g	4.8
DGA	134	100mM	~13.4 g	4.8
HCl	36.5 (35% assay)	2M	~200 mL	N/A

4.3.2 HPIC-ICPMS Preparation

In order to turn on the ICPMS, there are three prerequisites: verifying argon flow into the machine, securing the sample and waste tubing, and placing the sample tubing in a solution (most commonly 2% nitric acid). After the ICPMS turns on, and the plasma is lit, the machine needs to warm up for at least 10 minutes before performing any calibration or performance checks. At this time, the HPIC is turned on, at a flow rate of 0.5 mL/min of deionized water. Refer to Table 8 for both the ICPMS and HPIC operating parameters.

The next step is to perform an autotune routine through the Qtegra software using an Inorganic Ventures standard (Thermo-4AREV), which has a select group of elements (Ba, Ce, In, U, Bi, Co, and Li) at a concentration of 1 ppb (parts per billion, ng/g). During this autotune sequence, various parameters (such as nebulizer flow rate and torch position) of the ICPMS are optimized according to a user-specified autotune program for peak ICPMS operation. Next, a performance validation check is completed using the same 4A solution, which verifies that the operating parameters of the ICPMS fall within user-determined levels, such as the ICPMS sensitivity and oxide percentage generated within the plasma.

Once these calibration tests have been performed (and passed), the ICPMS is ready for sample analysis.

The next step before HPIC-ICPMS analysis is to prepare the HPIC column. First, the flow rate is changed to 1 mL/min. Second, if the HPIC has not been operated in several days, then the eluent lines should be primed using the Chromeleon software with each eluent at 25% and the pump valve open to direct to waste. This ensures that there are not any bubbles in the lines which will cause pressure drops and inconsistent separations. Running each eluent (or the combination thereof) also

Table 8. ICPMS and HPIC operating parameters.

Thermo Scientific Dionex ICS-5000+ HPIC	
PEEK injection loop volume	25 μ L
IonPac CG5A column	50 x 4 mm i.d.
	250 x 4 mm i.d.
IonPac CS5A column	Substrate 9 μ m particles
	40 μ equivalents/column
Eluent flow rate	1.0 mL/min
System pressure at 1.0 mL. min ⁻¹	~1600 psi
Post-column internal standard flow rate	0.1 mL/min
PEEK HPIC-ICPMS connection tubing	0.25 mm i.d.
Thermo Scientific iCAP-Q ICPMS	
Sampler cone diameter	1.1 mm
Skimmer cone diameter	0.5 mm
Plasma power	1549 W
Interface temperature	35.0C
Nebulizer gas flow rate	1.0 L/min
Axillary gas flow rate	0.78 L/min
Cool gas flow rate	13.95 L/min

strips the column from the previous samples' residues. Third, if samples containing high levels of uranium were analyzed the previous day, then the column should be stripped by running the HCl eluent for several minutes. During these processes, observations of the column pressure should be noted and monitored for outliers. Once all these steps are completed (if necessary), and the column pressure is steady and consistent with previous days' values, the HPIC-ICPMS system is ready to perform sample separation and analysis.

4.3.3 Microwave Dissolution Procedure

Any debris sample analyzed for this PhD project required a dissolution beforehand. The parameters programmed into the Milestone© microwave are given in Table 9, and the acid cocktail

prepared for each sample had a mix of nitric, hydrochloric, and hydrofluoric acids. The procedure for dissolution was:

- 1) Weigh out 100 mg (or 50 mg if sample has been through a torch or furnace) of the sample and note the final weight before placing in a clean microwave vessel
- 2) Repeat for all the samples
- 3) Pipet 10 mL of 8M HNO₃ in each vessel (and the vessel used as a blank with no sample)
- 4) Pipet 2 mL of concentrated HCl in each vessel (and blank)
- 5) Pipet 0.4 mL of concentrated HF in each vessel (and blank)
- 6) Close each vessel and torque to 22 N-m
- 7) Place in microwave and initiate the procedure given in Table 9
- 8) Once samples have cooled, verify that the samples have been fully digested
- 9) Pour final solutions in clean Falcon© tubes and bring up to either 20 or 35 mL (depending on the sample concentration)
- 10) Run a cleaning microwave run using 20–30 mL of 4M HNO₃ in each used vessel

Table 9. Microwave dissolution parameters

Time (min.)	Power (W)	Temp. (°C)
15	800	25–80
15	800	80
15	800	80–185
40	800	185

4.3.4 Sample Descriptions

4.3.4.1 Irradiated HEU

Several targets of highly-enriched uranium (HEU) were created for irradiation (see Figure 30) at the NACIL NAA facility, with the sample preparation described below.

Two HEU targets were prepared by evaporating portions of New Brunswick Laboratory certified reference standard U930-D (93.2% ^{235}U) into custom-made, high-purity silica ampoules 10 μL at a time for a total of 80 μL in each ampoule. After each 10 μL was added, a combination of a heat lamp and air flow over the ampoule openings was used to evaporate the nitric acid from the solution, causing the uranium to solidify as a nitrate salt at the bottom of each ampoule. Each of these steps is illustrated in Figure 30.

This technique was performed after the first round of samples (measuring 25–40 μL at a time into the ampoule and letting it air dry) proved to be time-consuming and not as accurate. Once all the necessary material was in the ampoules and dried, the ampoules were flame sealed by a member of the ORNL Nuclear & Radiochemistry group and sent over to the NAA lab for inspection before irradiation. After inspection, the ampoules were counted on HPGe detectors to quantify the fissile mass. Following the guidance of the Los Alamos National Laboratory Passive Non-Destructive Assay manual²⁰⁷, the 185.7 keV gamma was analyzed in background-subtracted spectra. The activity determined was divided by the specific activity of ^{235}U (79.8 kBq/g) to yield the total mass in each ampoule. For the set of samples created in 2017, the subsequent mass values were $30 \pm 3.5 \mu\text{g}$ and $80 \pm 5 \mu\text{g}$ for Targets 1 and 2, respectively²⁰⁸. The discrepancy between targets is likely due to partial evaporation of the HEU onto the neck of the ampoule, which is discarded during the flame sealing process.



Figure 30. Ampoule filled via syringe (left), solution dried by heat lamp and air flow (middle), final sealed targets of certified reference standard U930-D (93.2% ^{235}U) in high-purity silica ampoules²⁰⁸. Inset: scale in mm (right).

This experiment was performed twice, with the aforementioned samples in 2017 and one in 2018 (also 80 μg). The samples in 2017 were analyzed once as a proof-of-concept for RAPID, and the sample in 2018 was analyzed several times over the course of six weeks post-irradiation to monitor various isotopic decays and ingrowths.

CHAPTER 5: RAPID METHOD DEVELOPMENT

5.1 The RAPID Timeline

Originally, in 2014, NACIL was tasked to develop an HPIC-ICPMS technique for rapid analysis of low-level fission products of post-detonation nuclear forensics samples; thus, RAPID was created. In 2015, DTRA funded NACIL to continue these efforts, and subsequently, in 2017, tasked RAPID to provide analysis on an ORNL-developed surrogate melt glass project.

In an effort to test RAPID's abilities on irradiated HEU fission products (without a soil or glass matrix), HEU samples were generated for irradiation in the HFIR on ORNL campus.

Additionally, through some of this developmental work for RAPID, it was realized how complementary an inline gamma detection system would be to rapid fission product analysis with the HPIC-ICPMS, and a proof-of-concept setup was established and tested in 2019.

This chapter walks through the original method development of RAPID, including testing its robustness to matrices, particularly soil and surrogate melt glass, which are expected in post-detonation samples. The inline gamma detection system will be discussed in chapter 7.

5.2 Previous Work

Starting in 2015, the NACIL group began to develop the RAPID method in three stages: developing the separation chemistry, determining its stability and reproducibility, and measuring the limits of detection and quantification for multi-element samples with no matrix. Three different separation schemes were tried by varying the ion exchange column and choice of eluents before settling on the final selections described in the previous chapter. Figure 31 shows the initial separation scheme used to separate 26 elements in one run and Figure 32 illustrates the resulting

chromatogram. This separation was also tested with the actinides, and it was proved that the separation is viable for uranium, neptunium, and americium/curium (these elute at the same time) in addition to the lanthanides and various transition metals. Data detailing the stability, producibility, and limits of detection and quantification are published in an ORNL technical report⁸.

The next steps were to investigate the impact of a complex matrix on this separation, namely a soil matrix, as may be found in post-detonation debris (in a nuclear forensics scenario) and implement IDMS for more accurate analyses. The separation scheme was modified, adding a two-minute washing period of oxalic acid to elute additional contaminants from the resin after the main elution protocol and also extending the length (and concentration) of the DGA to accommodate the elution of tetravalent actinides (plutonium and thorium) and zirconium. This scheme is illustrated in Figure 33 and is the one used for the separations in section 5.3 with the exact percent and times detailed in Table 10.

To test the capability of RAPID paired with IDMS, and to prove that the resulting chromatographic peak areas (for elementally-separated analytes) can be used for isotopic analysis, a multi-element standard (IV-ICPMS-71A, 10 µg/mL or 10 ppm) was spiked with an isotopically-enriched lanthanide standard at a similar concentration created at ORNL. Three analyses were performed with RAPID for IDMS of those lanthanides, and final recoveries are given for each lanthanide (and each analysis) in Table 11. For ideal IDMS analysis (an uncertainty of 1–2%), the sample to spike concentration needs to be within an order of magnitude. This was the case for neodymium and samarium (see Table 11), but not for europium or gadolinium, and the resulting precision can be seen in the triplicate recoveries for each lanthanide. Europium and gadolinium most likely have a lower accuracy since the sample:spike ratio was not as close to one as it should have been.

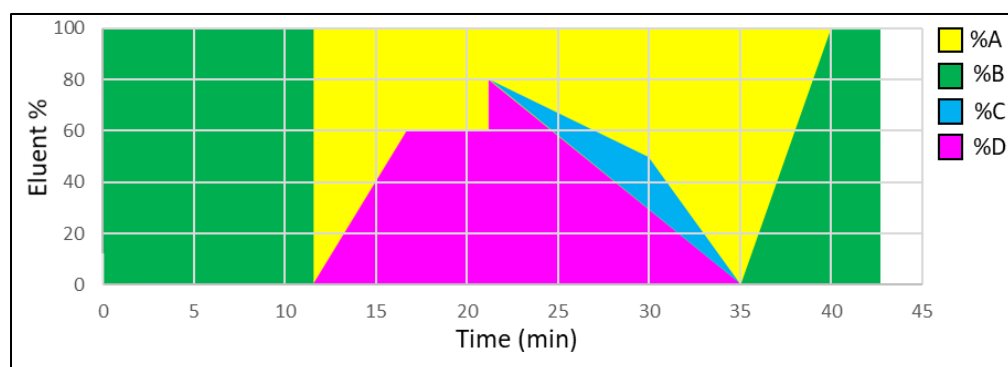


Figure 31. Separation scheme using deionized water (yellow/A), 6 mM PDCA (green/B), 100 mM DGA (blue/C), and 100 mM oxalic acid (pink/D)⁸.

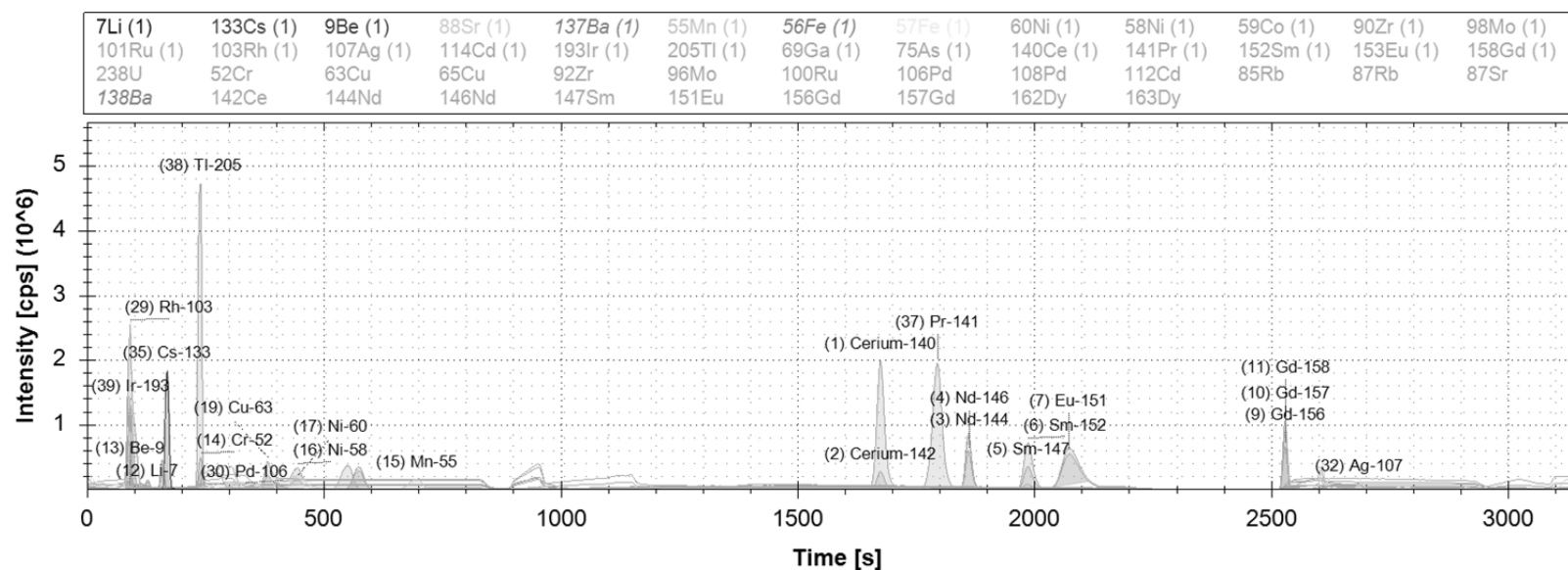


Figure 32. Resulting chromatogram of 26 elements after separation⁸.

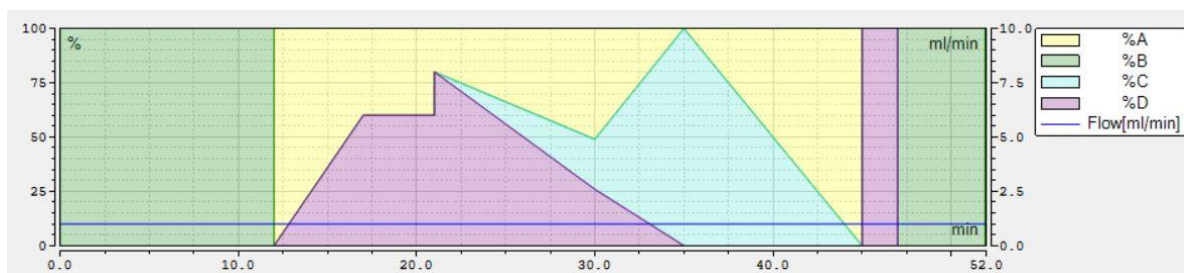


Figure 33. Modified separation scheme using deionized water (A), PDCA (B), DGA (C), and oxalic acid (D).

Table 10. Modified separation scheme elution profile.

Time (min)	Deionized H ₂ O (%)	PDCA (%)	DGA (%)	Oxalic Acid (%)
0	0	100	0	0
12	0	100	0	0
12.1	100	0	0	0
17	40	0	0	60
17.1	40	0	0	60
21	40	0	0	60
21.1	20	0	0	80
30	51	0	23	26
35	0	0	100	0
45	100	0	0	0
45.1	0	0	0	100
47	0	0	0	100
47.1	0	100	0	0
52	0	100	0	0

Table 11. Recoveries of the spiked lanthanides in IV-ICPMS-071A calculated with IDMS²⁰⁹.

	IDMS-A (%)	IDMS-B (%)	IDMS-C (%)	Recovery (%)	1 σ -SD (%)	Sample:Spike
Nd	99.8	99.8	99.1	99.6	0.8	1:1.11
Sm	99.8	101.0	99.0	99.9	0.9	1:0.35
Eu	108.1	90.5	100.4	99.7	7.8	1:0.03
Gd	99.0	105.9	102.8	102.6	3.3	1:0.04

Note: The entire IDMS procedure, including data interpretation, was performed in triplicate on two separate days. SD = standard deviation.

As can be seen, the separation does not affect the recovery of the IDMS process, and use of the peak areas for these analyses is suitable, as a <1% precision was obtained for neodymium and samarium. An illustration of the resulting neodymium peaks during this initial IDMS run is shown below in Figure 34, with the highest-abundance natural isotope (^{142}Nd) highlighted in red.

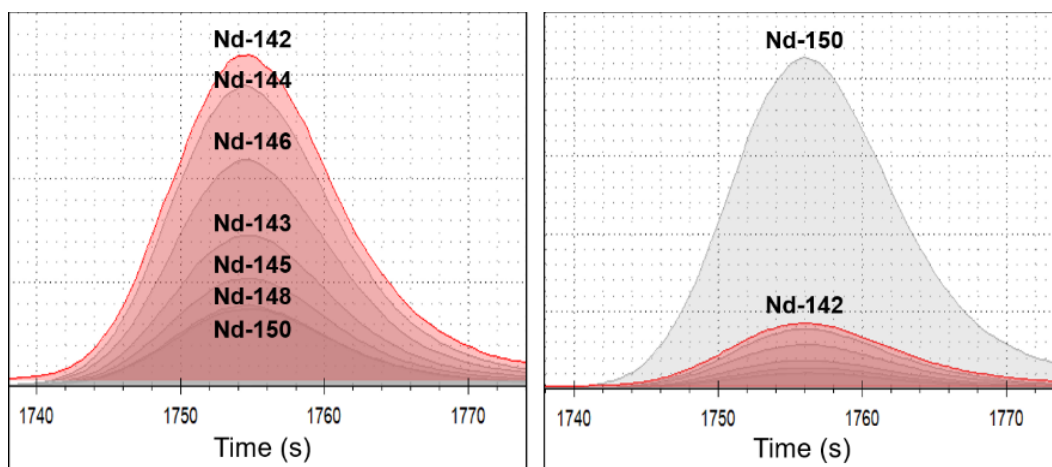


Figure 34. Resulting chromatograms of the natural neodymium standard (left) and the spiked neodymium standard (right) after separation²⁰⁹. Highlighted in red is the ^{142}Nd trace.

5.3 Separations in a Soil Matrix

In this section, a summary of the paper published in the Journal of Chromatography A will be given, followed by a more detailed methodology and results/discussion section of the initial RAPID method development for separations in a soil matrix.

5.3.1 Journal of Chromatography A Publication

Tested on a complex, silicon-based matrix, the method development, sensitivity, robustness, and uncertainties of RAPID are presented and discussed in this paper with the application to environmental samples. This method was unaffected by the matrix and yielded precise isotopic compositions for over 40 elements in one run, completed in under one hour, using an online separation-direct analysis scheme. When combined with IDMS, RAPID shows the ability to produce elemental concentrations with low uncertainties, rapidly analyzing group I/II metals, transition and refractory metals, platinum metals, lanthanides, and actinides.

This work presents the method development behind RAPID, from its elution scheme to the stability and isotopic detection limits of the method. To prove that chromatographic peak areas of elementally-separated analytes can be used for isotopic analysis, IDMS was performed with a multi-element standard and an ORNL lanthanide spike mix, resulting in a <1% accuracy and a <2% precision for two of the four lanthanides measured.

The sensitivity of this analytical method does not appear to be affected by a matrix, with limits of detection in the low picogram range (with and without a matrix). Several elements had detection limits in the femtogram range, which is not achievable with a quadrupole ICPMS using traditional analytical methods. Isotopic ratio precision and recoveries were also investigated during the detection limit study since IDMS relies on accurate ratios for quantification.

As a demonstration that RAPID's analysis is unaffected by complex matrices (due to the HPIC separation beforehand), a study was performed using IDMS on two samples with complex matrices: a trace-metals pure surrogate soil matrix created at ORNL and a NIST-certified reference material, 2711-a "Montana II soil standard". For these studies, the recoveries of selected lanthanides (cerium, neodymium, samarium, europium, and gadolinium) were calculated for both soils; notably, the NIST-certified soil has published values to compare to for these elements.

This work was published in the Journal of Chromatography A in 2018 and relevant results will be cited in section 5.3.3.

5.3.2 Methodology

To effectively perform analysis on nuclear forensics post-detonation materials, as well as other complex matrices, it was necessary to characterize the potential effect (or lack of) of a matrix on the chemical separation and subsequent method characteristics, such as limits of detection and analyte recovery. This effort began with creation of a surrogate soil designed after the NIST-certified Montana soil 2711a, with the composition given in Table 12. Once this surrogate was made, it was digested using the microwave dissolution detailed in section 4.3.3, spiked with several standards (IV-ICP-71A, IV-ICP-71B, IV-ICP-71C, and IV-ICP-71D), and analyzed with RAPID.

Within this analysis, the reproducibility and stability of the method, in addition to the limits of detection (LOD) and quantification (LOQ) for 48 elements, were assessed. Figure 35 illustrates the elements successfully separated from the corresponding isobaric interferences in addition to the elements expected in the matrices of melt glass and/or the acids used for dissolutions thereof. To test the stability of the method, nine replicates of spiked soil (at a concentration of 100 ppb) were analyzed twice, bracketed with blanks, which entailed running for ~24 h straight. From this, the relative standard deviation (RSD) was calculated, demonstrating the reproducibility over the

18 analyses and 24 h run time. It should be noted that each sample injection only consists of 50 μL of the sample (i.e. for a 1 ng/mL sample, only 50 pg is injected onto the column).

The LOD and LOQ for individual isotopes were calculated by measuring serial dilutions of the same multi-element standards as listed above: concentrations ranged from 1 ppt (parts per trillion, pg/g) to 10 ppb. The resulting peak areas of each isotope for each concentration were used to perform a least-squares linear regression analysis (employing the Microsoft Excel Analysis Toolpak regression function). The y-intercept from this analysis multiplied by 3.3 gives the LOD, while multiplication by ten gives the LOQ. Of note, several isotopes were excluded from this experiment because they existed within the surrogate soil matrix itself. In these cases, the LOD/LOQ can be calculated as $3.3\times/10\times$ of the standard deviation (SD) of the isotopic concentration in the soil blank, measured three times (seven replicates) over three non-consecutive days.

Additionally, IDMS was performed using this surrogate soil as a matrix to verify the quantitative ability of the RAPID method for IDMS of lanthanides and other selected metals (strontium, cadmium, and thallium). The lanthanide standards used were created in-house at ORNL in 2010, and the subsequently diluted concentrations are given in Table 13. Also listed in Table 13 is the concentration of the multi-element natural standard which was the “sample” in question to be spiked. The spikes are isotopically-enriched, listed alongside the element name below. Once the concentrations of both the spikes and sample were at 100 ppb, an aliquot of each was mixed at a 1:1 ratio. For the STP soil, two 40 mg aliquots were measured and digested; however, only one was used in this experiment.

* Lanthanide series

* * Actinide series

lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	euroium 63	gadolinium 64	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.905	140.12	140.908	144.24		150.36	151.964	157.25	158.925	162.50	164.930	167.26	168.934	173.054
actinium 89	thorium 90	protactinium 91	uranium 92	neptunium 93	plutonium 94	americium 95	curium 96						
Ac	Th	Pa	U	Np	Pu	Am	Cm						
227.033	232.038	231.036	238.029	237.048	244.064	243.061	247.065						

Elements Successfully separated from isobaric interferences
Elements expected in complex matrices

Figure 35. Graphical representation of the elements that have been successfully separated from isobaric interferences versus the elements expected in post-detonation debris or acids used for preparation of the material²⁰⁹.

Table 12. Surrogate soil composition, showing compounds used and elemental weight fractions²⁰⁹.

Element	Elemental weight fractions (%) and concentration (µg/g)
Si (Silicon dioxide, SiO ₂)	17.7 (750)
Al (Aluminum nitrate nonahydrate, Al(NO ₃) ₃ ·9H ₂ O)	3.7 (160)
Fe (Iron(III) oxide, Fe ₂ O ₃)	1.6 (70)
Ca (Calcium oxide, CaO)	1.3 (60)
Mg (Magnesium nitrate hexahydrate, Mg(NO ₃) ₂ ·6H ₂ O)	0.6 (30)

Table 13. Element concentrations for the IDMS analysis with the surrogate soil matrix.

Element (isotope)	Concentration (ppb)
Cerium (140)	100.77
Neodymium (150)	115.68
Samarium (152)	112.06
Europium (151)	114.28
Gadolinium (155)	110.92
Cadmium (106)	87.73
Thallium (203)	90.61
Strontium (86)	87.56
71A	99.98

Next, the NIST 2711a soil was spiked, digested, and then analyzed with IDMS to calculate the concentration of cerium, neodymium, samarium, europium, and gadolinium within the soil and fully test the performance of RAPID on a real soil matrix. The spike concentrations were intentionally designed to match the certified natural concentrations of the lanthanides present in the soil. The final concentrations of the spike and the naturally-abundant lanthanides in the soil are given in Table 14 for duplicate samples. The spike concentration was calculated by weighted dilutions from individual isotopically-enriched standards of each element listed, while the soil concentrations were similarly calculated through certificate values and weighted dilutions.

Table 14. Concentrations of the NIST 2711a soil and IDMS spike pre-dissolution.

Element (spike isotope)	NIST A		NIST B	
	Soil conc. (ppb)	Spike conc. (ppb)	Soil conc. (ppb)	Spike conc. (ppb)
Cerium (140)	109.7	131.3	111.1	133.6
Neodymium (150)	45.4	47.0	46.0	47.8
Samarium (152)	9.3	12.4	9.4	12.6
Europium (151)	1.7	2.3	1.7	2.3
Gadolinium (155)	7.8	9.8	7.9	9.9

5.3.3 Results and Discussion

Resulting chromatograms of the separation of the spiked surrogate soil are shown below in Figures 36–39. The initial chromatogram, Figure 36, illustrates the separation as a whole, while the following partial chromatograms highlight different sets of elements in closer detail. Figure 37 shows a partial chromatogram of two key fission elements: cesium (separated from its isobaric interference barium, $t = 90$ s) and strontium (separated from isobaric interferences yttrium, $t = 2010$ s, and zirconium, $t = 2280$ s). It can be seen in this partial chromatogram that ruthenium elutes at two different times – this is most likely due to a change in oxidation state, but the exact nature of the ruthenium is not known for this separation, and to confirm this, an additional study would have been required. Figure 38, a partial chromatogram of the transition metals, demonstrates the separation of iron from other first-row transition metals, such as copper, nickel, and cobalt, which can all be interferences on the iron signal depending on the isotopes analyzed in the sample. Of note, iron in the surrogate matrix was detected in addition to the iron standard, so the trace selected (^{58}Fe , 0.28% natural abundance) is seen at a similar concentration to the copper and nickel isotopes which exist at higher abundances. Lastly, Figure 39 shows the partial chromatogram of the lanthanide separation, which was unaffected by the addition of a soil matrix.

Next, retention times and overall stability of the method for each element (if measured) are given in Table 15, listing the shift in retention times for each element between no matrix and the surrogate soil matrix. Possible effects from sample matrices in an HPLC column include clogging (particulates), fouling (dissolved metals, organic compounds), and column overload (high concentrations causing peak suppression or nonlinear response). Any of these phenomena could cause a shift in retention times, given the amount and type of matrix. There is a slight shift in

retention times when the matrix is added; however, this is not a problem in this case, as it does not affect the separation from the isobaric interferences.

This shift in retention time is greater with the lanthanides than with the earlier metals, implying that it is occurring in the oxalic/DGA part of the elution profile. It is possible that the pH change of the oxalic acid as it ages (due to the buffering agent of ammonium hydroxide evaporating out of the solution over time) affects the lanthanide retention time. Analysis of a 100x dilution of the surrogate soil, focusing on the main matrix elements (silicon, iron, magnesium, aluminum, and calcium), showed that the majority elute at the solvent front, however, silicon and calcium (m/z 29 and 44 respectively) also exist in the eluents, most likely due to their organic components (probably $[\text{COH}]^+$ and $[\text{CO}_2]^+$ after ionization, respectively). This is illustrated in Figure 40, where the chromatograms of both m/z 29 and 44 follow the elution profiles, and this effect could be causing a slight shift in the lanthanides as the organics build up on the column.

The stability, determined by the relative standard deviation of nine separate runs over several days, shown in Table 15, varied from ~2% to 60% for a handful of elements. This stability is determined by the amount of the analyte (measured as counts) and most likely by the type of interaction between the analyte and the column. A high concentration of an element either not interacting at all with the column (thus eluting with the solvent front) or interacting in a very stable fashion (i.e. the lanthanides) should show much more stability and repeatability than another element/analyte that interacts inconsistently with the column.

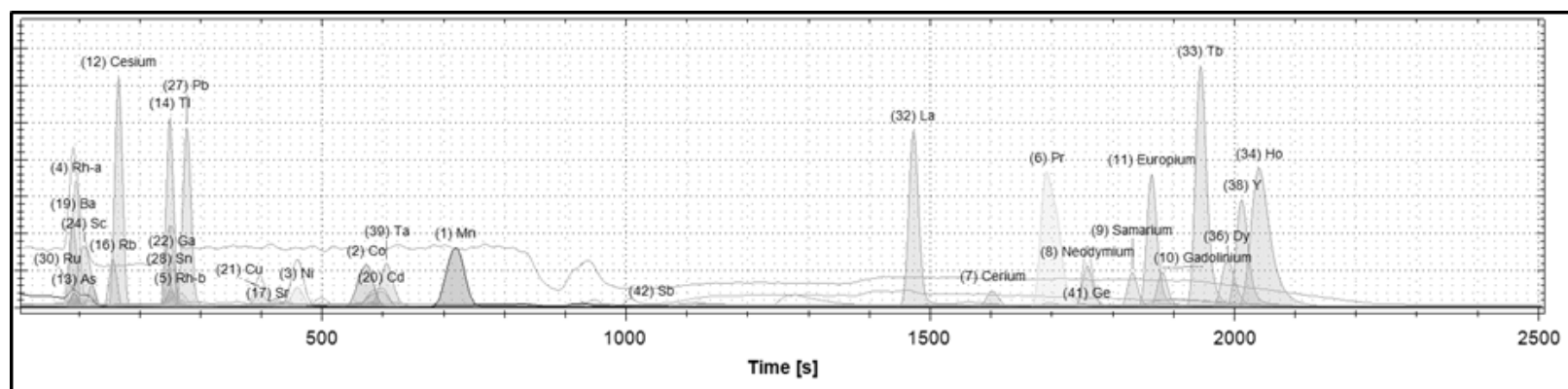


Figure 36. Chromatogram displaying 30 of the 48 elements monitored in a separation of a 100 ppb mix of standards in the surrogate soil matrix²⁰⁹.

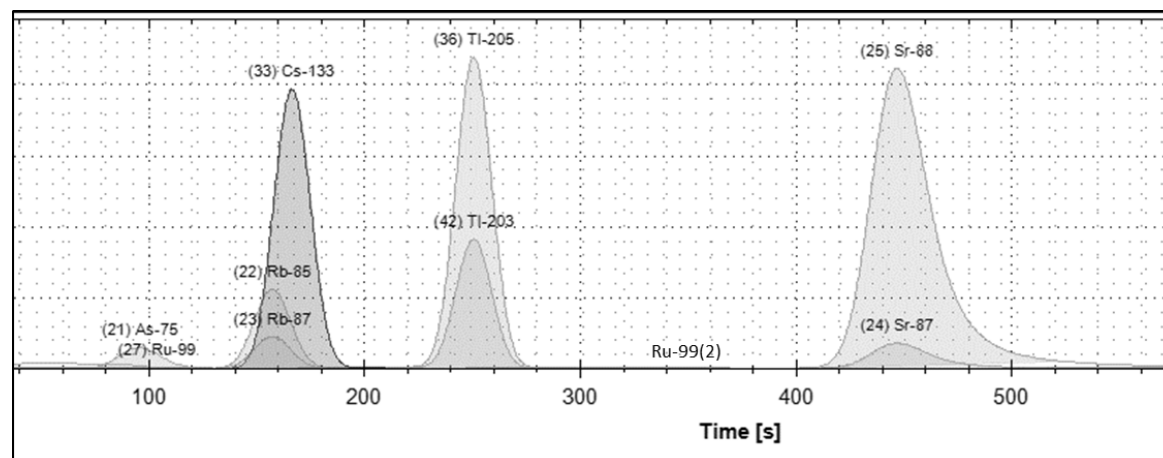


Figure 37. Partial chromatogram of Figure 28, illustrating separation of cesium and strontium from their isobaric interferences²⁰⁹.

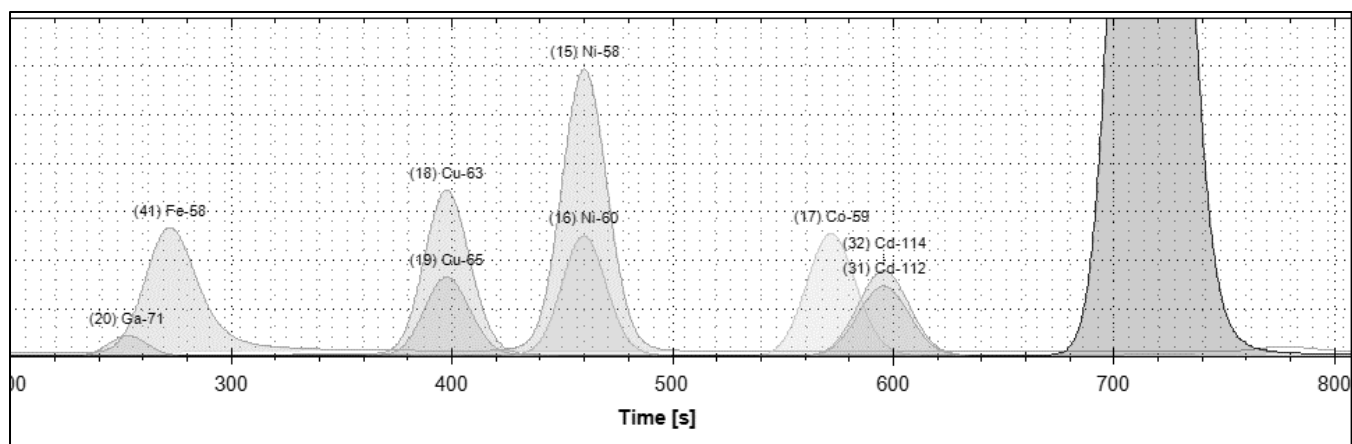


Figure 38. Partial chromatogram of Figure 28, demonstrating separation of iron from other first-row transition metals copper, nickel, and cobalt²⁰⁹.

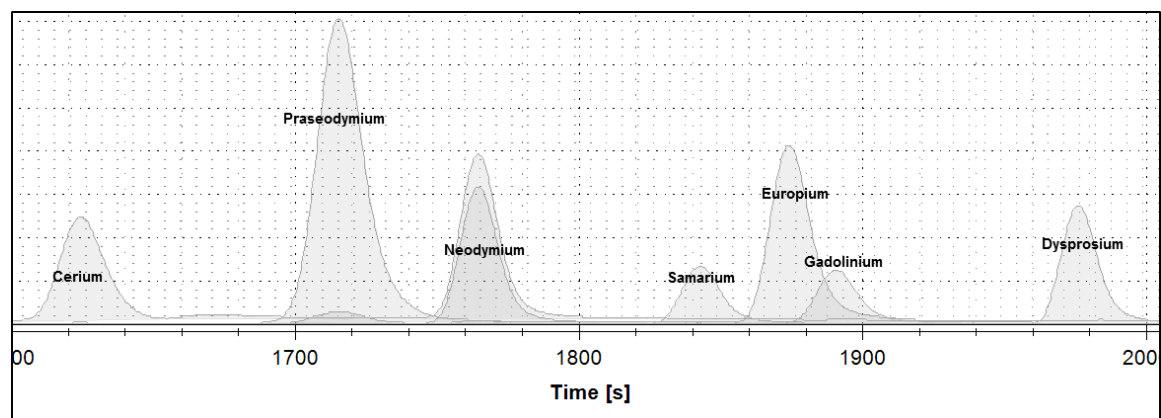


Figure 39. Partial chromatogram of Figure 28 showing clear separation of the lanthanides, unaffected by the addition of a soil matrix²⁰⁹.

Table 15. Stability and retention times in the surrogate soil matrix¹⁹⁸.

	Tracer	Retention time (s)		Shift due to matrix (s)	Stability over 24 h period (if measured) RSD 9 replicates (%)	Natural and non-natural isobaric interferences
		In surrogate matrix	In 5% HNO ₃			
Ba	¹³⁸ Ba	90	-	-	60.0	Ce, La, Nd
As	⁷⁵ As	92	-	-	6.8	-
Ir	¹⁹³ Ir	92	92	0	40.0	Re, Pt, Os
Se	⁷⁷ Se	92	-	-	59.0	-
Ru	¹⁰¹ Ru	100/350	130/400	-50	6.6	Rh, Pd, Cd, Ag
Te	¹²⁵ Te	100	-	-	5.2	-
Sc	⁴⁵ Sc	110	-	-	11	Ca, Ti, V
Np	²³⁷ Np	120	-	-	2.2	U
Nb	⁹³ Nb	123	-	-	6.2	-
Li	⁷ Li	126	129	-3	3.4	Be
Os	¹⁸⁹ Os	126	-	-	8.7	-
Rb	⁸⁷ Rb	157	161	-4	3.5	-
Cs	¹³³ Cs	165	190	-25	3.6	-
Tl	²⁰⁵ Tl	250	240	10	1.4	Ba, La, Ce
Sn	¹¹⁸ Sn	250	-	-	7.0	-
Ti	⁴⁹ Ti	251	-	-	N/A	-
Ga	⁷¹ Ga	253	-	-	4.6	Zn, Co
Rh	¹⁰³ Rh	270	-	-	21.0	Ru, Pd
Fe	⁵⁸ Fe	276	-	-	N/A	Cr, Mn, Co, Ni
Pb	²⁰⁸ Pb	278	-	-	2.1	Hg, Tl, Bi, Po
Zn	⁶⁶ Zn	296	-	-	N/A	Cu
Cu	⁶⁵ Cu	398	383	15	N/A	Zn, Ga
Pd	¹⁰⁵ Pd	427	411	16	N/A	-
Sr	⁸⁷ Sr	750	747	3	3.5	Y, Zr
Ni	⁶⁰ Ni	460	445	15	N/A	Fe, Cu, Zn
Co	⁵⁹ Co	575	553	22	40.0	Ni, Fe
Cd	¹¹² Cd	595	-	-	2.3	In
Au	¹⁹⁷ Au	606	-	-	7.9	Pt, Os, Ir, Hg
Ta	¹⁸¹ Ta	607	-	-	5.3	Hf, Re, W
Mn	⁵⁵ Mn	720	695	25	40.0	Fe
Sb	¹²¹ Sb	1020	-	-	6.2	-
La	¹³⁹ La	1473	-	-	3.0	-

Table 15 (cont.)

	Tracer	Retention time (s)		Shift due to matrix (s)	Stability over 24 h period (if measured) RSD 9 replicates (%)	Natural and non-natural isobaric interferences
		In surrogate matrix	In 5% HNO ₃			
Ce	¹⁴² Ce	1600	1675	−75	3.0	Pr, Nd, Sm, Pm
Pr	¹⁴¹ Pr	1692	1795	−103	3.2	Nd, Ce, Pm
Ge	⁷³ Ge	1750	-	-	5.7	-
Nd	¹⁴⁶ Nd	1760	1862	−102	2.5	Sm, Gd, Eu, Pm
Sm	¹⁴⁷ Sm	1830	1990	−160	2.0	-
Eu	¹⁵³ Eu	1865	2070	−205	1.8	Sm, Gd, Dy
Gd	¹⁵⁷ Gd	1882	2131	−249	3.4	-
Tb	¹⁵⁹ Tb	1945	-	-	3.0	-
Cm	²⁴⁴ Cm	1950	-	-	1.8	Am
Am	²⁴¹ Am	1970	-	-	1.7	Cm, Pu
Dy	¹⁶³ Dy	1990	-	-	1.7	-
Y	⁸⁹ Y	2013	-	-	5.0	-
Ho	¹⁶⁵ Ho	2,040	-	-	2.4	-
Pu	²³⁹ Pu	2250	-	-	10.0	Am, Cm
Th	²³² Th	2310	-	-	3.8	Ra, U
Tm	¹⁶⁹ Tm	2910	-	-	3.0%	-
Zr	⁹⁴ Zr	2280	-	-	4.9%	-

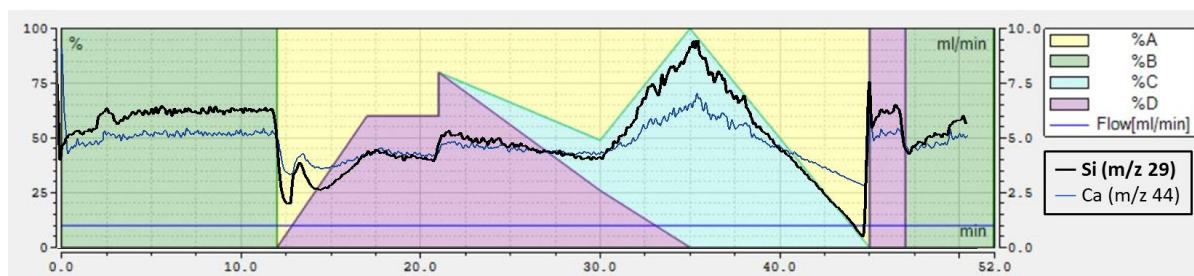


Figure 40. Elution profile overlaid with silicon and calcium chromatograms (normalized) from the surrogate soil and eluents, shown by the chromatograms following the shapes of the elution profiles.

Fully characterizing this phenomenon for each element presented in this study would require more knowledge of the nature of the species formed in each case; however, the effects of it can be seen in the resulting stability.

The resulting LODs/LOQs with and without the surrogate matrix are given in Table 16, showing that the main effect of the matrix on detection limits is when the isotope of interest is within the matrix background. Most of the isotopes measured in the surrogate soil matrix have an LOD similar to, or lower than, the LODs determined without a complex matrix. This is most likely due to the fact that the original LOD study used higher concentrations of standards (2500 pg vs 500 pg), weighting the linear regression high and skewing the calculated LODs. Certain elements monitored in the previous study were not monitored in this matrix study because they existed in the soil matrix in levels higher than the determined detection limits. Others, such as ^{142}Ce , were monitored, but due to their existence in trace-levels in the soil, were determined to have a higher LOD than in the previous study. Overall, these detection limits, on average in the low picogram range, are lower than that of a typical quadrupole ICPMS, illustrating the benefit of adding the online separation capability to an ICPMS. Additionally, the injection and subsequent concentration of each element on the column as it separates provides a higher intensity going into the ICPMS and thus a lower detection limit than offline ICPMS.

Recoveries from the IDMS test with the surrogate soil are listed in Table 17, and all elements eluted properly except for cadmium. The lowest recovery of these is cerium, which is probably due to it being a natural contaminant in the eluents. This is surprising, given that the cerium spike to sample concentration was the closest to 1:1, compared to all of the other spikes, which ranged from a spike/sample ratio of ~ 0.85 to ~ 1.2 . It can also be seen that cerium has the lowest uncertainty, which is most likely due to its spike/sample ratio of 1. Including uncertainties, all the

Table 16. Isotopic LOD/LOQs with and without the surrogate soil matrix¹⁹⁸.

Isotope	LOD (pg) (no matrix)	LOD (pg) (surrogate soil matrix)	LOQ (pg) (no matrix)	LOQ (pg) (surrogate soil matrix)	Comments
⁷ Li	48.4	-	146.5	-	Matrix Bkg
⁸⁵ Rb	7.0	1.6	21.1	4.7	-
⁸⁷ Rb	2.8	-	8.6	-	Not Analyzed
¹³³ Cs	8.5	1.6	25.7	4.8	-
⁸⁷ Sr	4.0	-	12.2	-	Not Analyzed
⁸⁸ Sr	37.1	-	112.4	-	Matrix Bkg
⁵⁵ Mn	83.6	-	253.2	-	Matrix Bkg
⁵⁹ Co	14.1	-	42.6	-	Matrix Bkg
⁵⁸ Ni	169.7	-	514.1	-	Matrix Bkg
⁶⁰ Ni	76.4	-	231.6	-	Matrix Bkg
⁶³ Cu	109.5	-	331.8	-	Matrix Bkg
⁶⁵ Cu	43.5	-	131.8	-	Matrix Bkg
⁶⁹ Ga	21.4	-	64.8	-	Not Analyzed
⁷⁵ As	19.4	-	58.7	-	Not Analyzed
²⁰⁵ Tl	12.0	0.7	36.4	2.2	-
¹⁰⁰ Ru	5.0	-	15.2	-	Not Analyzed
¹⁰¹ Ru	5.6	6.6	17.0	20.1	-
¹⁰³ Rh	16.6	1.3	50.2	3.9	-
¹⁰⁶ Pd	6.5	-	19.7	-	Not Analyzed
¹⁰⁸ Pd	2.8	-	8.5	-	Not Analyzed
¹¹² Cd	5.9	1.9	17.8	5.9	-
¹¹⁴ Cd	7.2	1.0	21.9	2.9	-
¹⁹³ Ir	6.3	1.1	19.1	3.3	-
¹⁴⁰ Ce	8.1	7.6	24.6	22.9	High Bkg
¹⁴² Ce	0.6	8.1	1.8	24.7	High Bkg
¹⁴¹ Pr	25.9	0.5	78.5	1.5	-
¹⁴² Nd	0.4	0.7	1.2	2.1	-
¹⁴⁴ Nd	1.8	0.7	5.6	2.0	-
¹⁴⁶ Nd	1.3	1.3	3.9	3.9	-
¹⁴⁷ Sm	2.2	1.5	6.6	4.5	-
¹⁵² Sm	5.2	1.1	15.8	3.3	-
¹⁵¹ Eu	1.3	0.8	4.0	2.3	-
¹⁵³ Eu	2.0	1.0	6.0	3.0	-
¹⁵⁶ Gd	2.5	0.8	7.7	2.5	-
¹⁵⁷ Gd	2.3	1.3	7.1	4.0	-
¹⁵⁸ Gd	2.2	0.9	6.7	2.8	-

elements (except for cerium) were recovered at 100%. From these results, it can be expected that a soil matrix will not affect the ability for full recovery of lanthanides, strontium, and thallium in any subsequent IDMS analysis.

IDMS performed on the NIST 2711a soil gave values that matched the certificate values; notably, RAPID allowed for accurate analysis of all the lanthanides with one technique, while the NIST ICPMS analysis only provided one value (cerium). Additionally, without the separation that RAPID provides, the CeO (with both ^{140}Ce and ^{142}Ce) would have caused a polyatomic interference on the gadolinium signal (m/z 155 and 157, respectively) seen using traditional mass spectrometry.

Table 18 lists all the values obtained with RAPID (two-sigma standard deviation) and from the NIST certificate, and the variance in the NIST values demonstrates the tenacity of the sample matrix and its effect on the accuracy of the analyses. This IDMS analysis yielded a 1–3% precision, which is comparable to the precision obtained without the soil matrix. Similar to the surrogate soil study, cerium is the outlier in this study, with its precision lower than the other elements. This may be due to natural contamination in the eluents or an issue with the dissolution of the soil – the NIST report on the analysis of 2711a confirms issues acquiring consistent cerium values. Samarium is the only NIST-certified value, and the RAPID measurement yielded a better precision in addition to falling within the uncertainty of the NIST NAA analyses. Neodymium and europium, both NIST reference values, also showed higher precision than the NIST analysis and fell well within its uncertainty. Lastly, cerium and gadolinium were only provided as information values on the certificate, and RAPID still matched those values. Overall, RAPID's successful analysis of this NIST reference material demonstrated its utility and precision for lanthanide

Table 17. Final recoveries of the spiked elements within the surrogate soil matrix.

Element	Recovery	2 σ STD
Cerium	92.03%	1.71%
Neodymium	98.8%	2.2%
Samarium	102.1%	2.7%
Europium	100.42%	2.69%
Gadolinium	97.9%	2.4%
Strontium	102.69%	2.24%
Thallium	100.79%	2.37%

Table 18. RAPID IDMS values compared to NIST certified values of SRM 2711a soil.

Analytical Technique	Ce ($\mu\text{g/g}$)	Nd ($\mu\text{g/g}$)	Sm ($\mu\text{g/g}$)	Eu ($\mu\text{g/g}$)	Gd ($\mu\text{g/g}$)
RAPID A (2 σ STD)	70(3)	32.5(4)	6.1(1)	1.10(5)	5.0(1)
RAPID B (2 σ STD)	75(2)	33.5(4)	6.2(1)	1.14(2)	5.1(1)
Average (2 σ STD)	72(5)	33(1)	6.15(10)	1.12(4)	5.05(6)
SRM 2711a Certificate Value	70*	29(2)#	5.93(28)¥	1.1(2)#	5*
INAA (2 σ STD)	77(4)	32(4)	6.1(5)	1.10(2)	5.1(1)
PGAA (2 σ STD)	-	-	5.82(8)	-	-
ICP-MS (2 σ STD)	66(2)	-	-	-	-
ICP-AES (2 σ STD)	66(2)	30(2)	-	-	-
ED-XRF (2 σ STD)	62(6)	26(10)	-	-	-

¥Certified Value, #Reference Value, *Information Value

measurement within a complex soil matrix, and the entire process (spiking, dissolution, measurement, and data processing) was performed in under 12 hours.

5.4 Separations in a Surrogate Debris Matrix

5.4.1 Methodology

Several iterations of the ORNL surrogate debris were given to NACIL for analysis in 2018, most of which were merely spiked with uranium. As no separations are necessary for the quantification of uranium, offline ICPMS was used for these samples; however, they were used as a matrix for

other experiments as both soil/zeolite and uranium are constituents. As part of the DTRA project involving both RAPID development and the ORNL surrogate debris, a round robin was designed and completed in August 2018. The goal: ORNL creates surrogate debris with fission products obtained through uranium irradiation at HFIR, then other laboratories (including NACIL) analyze the debris with a rapid turnaround (timeline is shown in Figure 41). This compressed timeline between sample creation and analysis demonstrates what the forensics community looks for in its analytical capabilities.

Subsequently, 30 μg of HEU was irradiated in HFIR through the NAA laboratory, the target broken and leached (by the PER group), then the solution added to the debris creation process detailed in section 1.4.1. The samples were received by NACIL for analysis and included the leach solution, the debris pre-torch, and the debris post-torch.

The next study performed for method development was another LOD/LOQ study, following the same process as the earlier studies (section 5.3.2), but with a dissolved ORNL surrogate debris as the matrix to assess how it affects the overall LODs. Understanding any changes in the limits of detection within a surrogate melt glass debris matrix would be applicable in a post-detonation nuclear forensics analysis scenario.

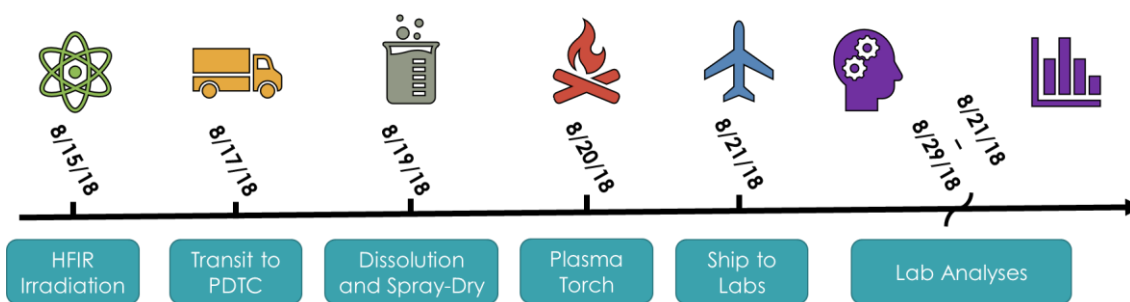


Figure 41. August 2018 round robin timeline for ORNL.

For this LOD/LOQ study, a series of multi-element standards (IV-71ABCD) were analyzed with a 10-fold dilution of a dissolved ORNL matrix (TR-103D), with a column loading ranging from 0.5 pg to 125 pg. Analysis was performed on two non-consecutive days with the same sample list:

- Five replicates of the matrix blank (10x TR-103D)
- Two replicates of 0.01 ppb (0.5 pg loading) standards in matrix
- Matrix blank
- Two replicates of 0.05 ppb (2.5 pg loading) standards in matrix
- Matrix blank
- Repeated for 0.1, 0.5, 1, and 2.5 ppb standards

Once the data was acquired, the same process of analysis with Excel and its linear regression tools were used to calculate the LOD and LOQ for each isotope of each element, focusing on major fission products (Y, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb).

The last method development experiment was dissolution and analysis of UT surrogate debris to further test RAPID's ability to handle complex matrices during a separation. Two samples in duplicate were digested at the same time, one of the "Houston v3" composition in a crushed powder form (masses of 0.0447 g and 0.0519 g), and one of the "NYC v2" composition, where both duplicates had two pieces of sample (masses of 0.0571 g and 0.0623 g). The dissolution detailed earlier was completed three times in a row for these samples, with 100 μ L additional HF added to the final iteration to try and further aid the dissolution. Other dissolution protocols would have been performed and assessed for this material, however, that was not part of the scope of this dissertation work (see previous work on dissolution of this material by another graduate student for comparable results²¹⁰).

The first analysis performed on these samples (using a 2500x) was offline ICPMS to estimate the recovery of the dissolution, focusing on matrix elements (to compare to the other graduate work previously mentioned). Secondly, 10x-diluted aliquots from each dissolved sample were spiked with a weighed mix of isotopically-enriched and natural standards for selected lanthanides (cerium, neodymium, samarium, europium, and gadolinium) to perform IDMS. A spike mix of these lanthanides was created, with concentrations ranging from 100–110 ppb (see Table 13); respectively, the natural standard concentration was made at 100 (97.5) ppb. From this point, these two solutions were mixed at a 1:1 ratio and diluted to an approximate 20 ppb in the final solution for analysis. For each matrix (HOU and NYC), a blank, a matrix blank, a 20-ppb natural standard, and four replicates of the spiked matrix, four replicates of the mix, and four replicates of the natural standard in the matrix (each set bracketed by matrix blanks) were run through RAPID. Once these samples were analyzed, and IDMS calculated performed, it will be seen whether the dissolved surrogate matrix affects the recovery of lanthanides through IDMS.

5.4.2 Results and Discussion

Unfortunately, it was discovered that the PER leaching process was not particularly efficient, and very little of the generated fission products were in any of the samples (~0.2% calculated retention between the irradiated sample and the leachate). All the resulting samples were analyzed with RAPID, but due to this low retention, the debris samples had no measurable fission products above the detection limits. Each of the debris samples had even fewer fission products than the previous sample (leachate > pre-torch debris > post-torch debris), which was measured with HPGe in lieu of RAPID for the round robin results reported to the sponsor. However, the next chapter will demonstrate RAPID's capability for analyzing freshly-generated fission products following a more robust leaching methodology.

For the LOD/LOQ study with the ORNL surrogate debris as a matrix, a smaller set of elements was analyzed compared to the original studies, which looked at over 40 elements. Fission product elements yttrium, cesium, and the first half of the lanthanides (which will be the most prominent in an irradiated sample) were analyzed in duplicate at concentrations ranging from 0.01 ppb to 2.5 ppb. The resulting LODs and LOQs for each isotope are listed in Table 19, ranging from 500 fg (^{159}Tb) to ~17 pg (^{152}Gd , 0.2% natural abundance). Even with the contamination in the matrix (i.e. non-zero values of the lanthanides being analyzed existing in the matrix blank) used, which produces a more conservative estimate of these limits, they are fairly low and comparable to the earlier results.

Figure 42 illustrates a comparison of all three detection limit studies performed with RAPID: the original study with no complex matrix, the second study in a clean surrogate soil matrix (no contaminants), and this study in a more realistic, contaminated matrix. The calculations for each LOD/LOQ study were performed the same way in Excel, as given in section 5.3.2. The other important difference between these LOD studies (other than the matrix) were the column loading ranges of the standard analyzed. For the very first study, the highest column loading was 2500 pg, while the second study (surrogate soil matrix) went up to 500 pg, and this study's highest loading was 125 pg. The 2500 pg loading caused the linear regression calculation to become biased high, and thus the LOD/LOQs were higher than they should have been, most notably with cerium and ^{152}Sm . As seen in Figure 42, small differences can be observed, but overall, RAPID's detection limits of these isotopes are in the low picograms, no matter the matrix.

To prepare the next set of debris samples for analysis, the solutions of both the UTK-generated Houston and NYC samples were brought up to 20 mL after the final dissolution was completed.

Table 19. Detection limit study results in a contaminated ORNL surrogate debris matrix.

Isotope	LOD (pg)	LOQ (pg)
⁸⁹ Y	5.01	15.19
¹³³ Cs	2.41	7.30
¹³⁹ La	2.57	7.78
¹⁴⁰ Ce	1.69	5.11
¹⁴² Ce	2.10	6.37
¹⁴¹ Pr	2.48	7.51
¹⁴² Nd	2.27	6.89
¹⁴³ Nd	2.09	6.34
¹⁴⁴ Nd	2.01	6.09
¹⁴⁵ Nd	2.08	6.31
¹⁴⁶ Nd	2.04	6.18
¹⁴⁸ Nd	2.49	7.54
¹⁵⁰ Nd	3.46	10.49
¹⁴⁴ Sm	1.68	5.09
¹⁴⁷ Sm	1.80	5.45
¹⁴⁸ Sm	1.17	3.56
¹⁴⁹ Sm	1.32	4.00
¹⁵⁰ Sm	1.75	5.31
¹⁵² Sm	1.96	5.95
¹⁵¹ Eu	0.81	2.47
¹⁵³ Eu	0.83	2.50
¹⁵² Gd	16.78	50.85
¹⁵⁴ Gd	5.03	15.23
¹⁵⁶ Gd	2.10	6.35
¹⁵⁷ Gd	1.58	4.78
¹⁵⁸ Gd	2.40	7.26
¹⁶⁰ Gd	2.06	6.23
¹⁵⁹ Tb	0.58	1.75

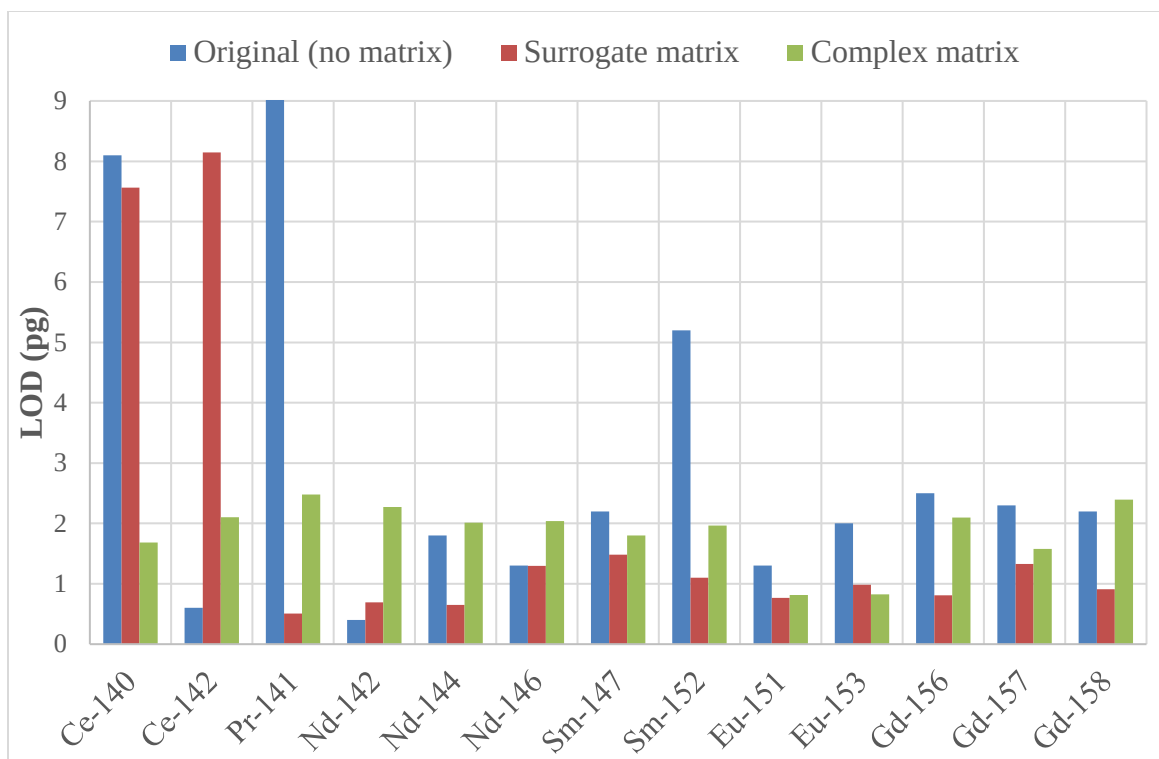


Figure 42. Limits of detection for the lanthanides from three different detection limit studies performed with RAPID with three different matrices (nitric acid, clean surrogate soil, and complex ORNL surrogate debris).

None of the four samples went completely into solution; notably, the NYC samples with the larger solids appeared to go into solution better than the powdered Houston samples. If this PhD were focused on dissolution of post-detonation debris, then a secondary study would have been performed further optimizing this process; however, the estimated recoveries here matched those given in a previous student's work purely focused on this dissolution process²¹⁰. In each sample post-dissolution, there were small black particles, which may be carbon from the graphite crucibles used during the surrogate formation process. To estimate the recovery of the dissolution, the calculated (and subsequently normalized) weight percentages were compared to the original compositions¹⁰, shown in Table 20. The measured compositions are roughly similar to the original composition, with the exception of a few elements (Fe, Ca, K) that may differ in dissolution rates

and/or have interferences in the ICPMS ($\text{ArO}^+ / ^{56}\text{Fe}$, $^{40}\text{Ar} / \text{Ca/K}$) during analysis that may cause incorrect measurements. It was calculated that this dissolution method (which takes < 2 h) resulted in approximately 5% recovery with a ~5% precision of the offline ICPMS analysis. This recovery is close to that obtained by Gill during his aforementioned study of the dissolution of these particular melt glasses²¹⁰, thus, it was assumed that this would be a realistic comparison to what a national lab could achieve in a quick-turnaround dissolution of post-detonation debris in a nuclear event scenario.

Once the debris samples were in solution, the next experiment was a test of the recovery of selected lanthanide spikes via IDMS as described in section 5.4.1. The purpose of this test was to demonstrate whether or not the additional matrix of melt glass in a post-detonation sample scenario would affect the ability to use IDMS for lanthanide analysis with RAPID. If the matrix was found to severely impact the recoveries of the lanthanides, then more sample preparation (i.e. filtering, a secondary guard column, etc.) would be necessary before analysis of a sample in that nuclear forensic capacity. However, if the matrix does not affect this analysis (as the previous matrices have not), then RAPID can be presented as a robust method useful for screening post-detonation samples.

The calculated recoveries of these lanthanides are presented in Table 21 with the standard deviations calculated with the associated precision of the analysis, varying from 89–106%. Of note, as was noticed in the ORNL debris, there was also natural lanthanide contamination in these samples, which affected these results (e.g. europium has >100% recovery), since the UTK radiochemistry laboratory does not use trace-metals pure grade chemicals that are necessary for low-level ICPMS analysis. For comparison, the surrogate soil created at ORNL had <400 counts of $^{151}\text{Eu} / ^{153}\text{Eu}$ (and 100% recovery with IDMS) whereas the NYC-001 UTK sample had ~2500k

counts of $^{151}\text{Eu}/^{153}\text{Eu}$. However, when these current IDMS recoveries are compared to earlier IDMS results from the surrogate soil study (see Table 17), these recoveries are not substantially different, which demonstrates that this more complex, contaminated matrix did not strongly affect this analysis. These recoveries are not ideal for a precise IDMS analysis, but in a real post-detonation nuclear forensics scenario, RAPID would be used to quickly screen samples, and higher fidelity analyses could be performed on a more sensitive machine after additional sample purification has been completed. Overall, the entire process (dissolution through data analysis) was completed in less than 24 h.

Table 20. Original debris composition compared to the measured composition post-dissolution with offline ICPMS analysis.

Original composition (w%)			Measured composition (normalized w%)				
	NYC	HOU		NYC-001	NYC-002	HOU-001	HOU-002
SiO ₂	60.49	63.71	Si	69.3%	68.1%	58.0%	59.3%
Al ₂ O ₃	15.1	17.88	Al	17.1%	17.9%	28.6%	27.3%
Fe ₂ O ₃	7.63	6.22	Fe	5.8%	6.7%	6.3%	7.2%
CaO	6.35	7.47	Ca	2.6%	2.6%	4.1%	3.7%
KOH	3.55	2.2	K	0.6%	0.2%	-	-
MgO	2.65	0.87	Mg	2.9%	3.0%	1.7%	1.4%
BaO	0.06	0.09	Ba	0.1%	0.1%	0.3%	0.1%
MnO	0.12	0.06	Mn	0.1%	0.1%	0.1%	0.1%
TiO ₂	0.61	0.6	Ti	0.6%	0.7%	1.0%	0.9%
UNH	0.06	0.06	U	0.9%	0.5%	-	-

Table 21. IDMS recoveries of selected lanthanides in both UTK surrogate debris matrices.

	HOU1	2 σ	NYC1	2 σ
Ce	89.3%	0.7%	89.2%	0.8%
Nd	93.3%	1.0%	91.6%	1.4%
Sm	96.6%	2.0%	95.3%	2.1%
Eu	100.7%	2.0%	106.2%	3.5%
Gd	87.4%	2.1%	87.2%	1.8%

CHAPTER 6: IRRADIATED FISSION PRODUCT ANALYSIS WITH RAPID

This chapter will describe the steps taken to apply RAPID to nuclear forensic analysis, and the overall goal of this work is to prove RAPID's capability to rapidly analyze freshly generated fission products.

The first two sections will summarize the papers published on this work, in the Journal of Radioanalytical and Nuclear Chemistry (JRNC) and Talanta, respectively.

6.1 JRNC Publication

The application of RAPID to irradiated HEU is presented in this paper, demonstrating that it has the sensitivity and precision required for low-level analyses of non-natural isotopes present in irradiated nuclear material. Fission product isotopic ratios were successfully measured at the low-picogram level, with a bulk uranium matrix present, and the measured ratios matched predicted ratios from an isotopic depletion and decay modeling software.

Two HEU targets (30 μg and 80 μg) were irradiated at ORNL to generate fission products for analysis, and the ORIGEN modeling software was used to predict the subsequent fission product inventory for comparison and recovery calculations. After irradiation, both targets were leached with nitric acid then analyzed with RAPID, specifically the elements strontium, ruthenium, cesium, cerium, neodymium, and samarium.

Successful separation was observed between each of these elements and their isobaric/polyatomic interferences (i.e. strontium and yttrium, cesium and barium, cerium and neodymium), which allowed for accurate isotopic ratio measurement. Comparison with ORIGEN models resulted in

recoveries ranging from 85–102% from the original, predicted ratio to the measured ratio with RAPID. On average, there was only 1–2% deviation from the measured ratio to the predicted ratio, even given that the analyzed masses of each of these elements were in the sub-picogram range, demonstrating RAPID's sensitivity and accuracy. No effects from the uranium matrix were seen during this analysis besides a slight shift in the elution times of some of the fission products. Lastly, this demonstrates RAPID's capability for rapid and accurate analysis of fission products soon after irradiation.

6.2 Talanta Publication

In this study, RAPID was used to analyze HEU fission products rapidly after irradiation and to monitor subsequent decay and ingrowth of nine key fission products during the six weeks post-irradiation. Isotopic concentrations were determined using RAPID for all key fission products, and gamma spectroscopy (with HPGe) confirmed the concentration of a few short-lived fission-generated isotopes.

An 80 µg HEU target was irradiated at ORNL for one hour, generating approximately 10^{14} fissions, then leached with nitric acid and analyzed with RAPID 178 hours after irradiation. Two additional analyses were performed at 504 and 1018 hours to monitor the shift in isotopic composition as shorter-lived isotopes decayed and grew in accordingly. Measurements of the irradiated material with an HPGe detector confirmed the concentration of six short-lived isotopes to within 1–6% of the RAPID ICPMS measurements at 178 h.

It was observed that only ~60% of the mass predicted by ORIGEN was measured in each analysis: another modeling software was used to predict that the fission products penetrate the silica ampoule to an average depth of 25 µm. From this, it was assumed that incomplete recovery

occurred due to the leaching process not accommodating for the resulting penetration into the ampoule. A secondary leach with nitric acid was performed on the ampoule, and an additional 15% recovery was measured, confirming this hypothesis.

The precision and sensitivity of RAPID as applied to non-natural isotopes (fission-generated vs. naturally abundant) analyzed within a uranium matrix is shown in this study. Isotopic compositions of key fission product elements cesium, strontium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, and samarium were determined less than 200 h after irradiation and matched ORIGEN predictions within 1-2% (even with some analyzed masses in the femtogram range). Notably, the shift in masses 143 (cerium, promethium, neodymium) and 147 (neodymium, promethium, samarium) as a function of time after irradiation was successfully observed and measured with RAPID. This is significant because these elements existed at a low-level mass range (femtogram to picogram) after irradiation and had isobaric interferences. Additionally, the observation of these still-decaying low-level fission products demonstrates the importance of a rapid analytical technique for a thorough characterization of the irradiated material.

6.3 Methodology

6.3.1 Nuclear Material Characterization and Sample Preparation

Before irradiation, it was necessary to characterize the starting material for any existing lanthanide contamination; if there is, it can be compensated for after irradiation and analysis. Initially, both uranium and plutonium were going to be irradiated and analyzed; however, only uranium was successfully irradiated for this dissertation and will be the focus of this chapter. The uranium standard used was U930-D CRM (enriched 93% ^{235}U). Due to the radioactivity limits imposed by the NAA facility, the uranium samples were limited to 80 μg ^{235}U . To properly emulate these final samples going into the HFIR, a blank (unirradiated) sample was created to generate a similar mass

and dilution profile of the dissolution post-irradiation (3 mL 4M nitric acid). The sample was created with 70 μ L of U930-D in 3 mL of 4M nitric acid. The sample was diluted with water (2x), as it was discovered that the retention time is affected by the concentration of the nitric in the final sample. The uranium was externally calibrated with a 2.5 ppb standard of the lanthanides and was analyzed in triplicate with RAPID.

6.3.2 ORIGEN Modeling

The next step was to prepare the uranium samples for irradiation, which is detailed in section 4.3.4. Once this was finished, and the ampoules accepted for irradiation, an ORIGEN calculation was completed to determine the necessary irradiation time to generate $\sim 10^{14}$ fissions. The number of fissions was chosen for two reasons. First, this number of fissions approaches what a real sample may be in a nuclear forensics post-detonation scenario, and second, the yield of fission products was estimated to be above the detection limits for the RAPID method (see Figure 43). This plot was generated with ORIGEN and illustrates the masses of each fission product as a function of time after irradiation. Dependent on ^{235}U mass, the irradiation times for the samples to reach 10^{14} fissions varies from 50 minutes (80 μ g) to five hours (30 μ g), and decay times may vary from a few days to weeks, depending on the radioactivity of the sample and the limits of the receiving facility.

Over the course of this work, three HEU targets were created, irradiated, and analyzed with RAPID. Targets 1 and 2 were created and irradiated at the same time with ^{235}U masses of 30 μ g and 80 μ g respectively, and Target 3 was created (80 μ g ^{235}U) and irradiated later. Results from Targets 1 and 2 were influential to the generation of Target 3, and ORIGEN was used for prediction and comparison of fission products each time. Once the exact mass and irradiation parameters were known, exact decay times were input to ORIGEN for precise comparisons, appropriately

compensating for the fission product decay. General irradiation and decay details are given in Table 22. The specific irradiation and decay details used for the ORIGEN modeling are given in Table 23. An example ORIGEN input file is given in the appendix.

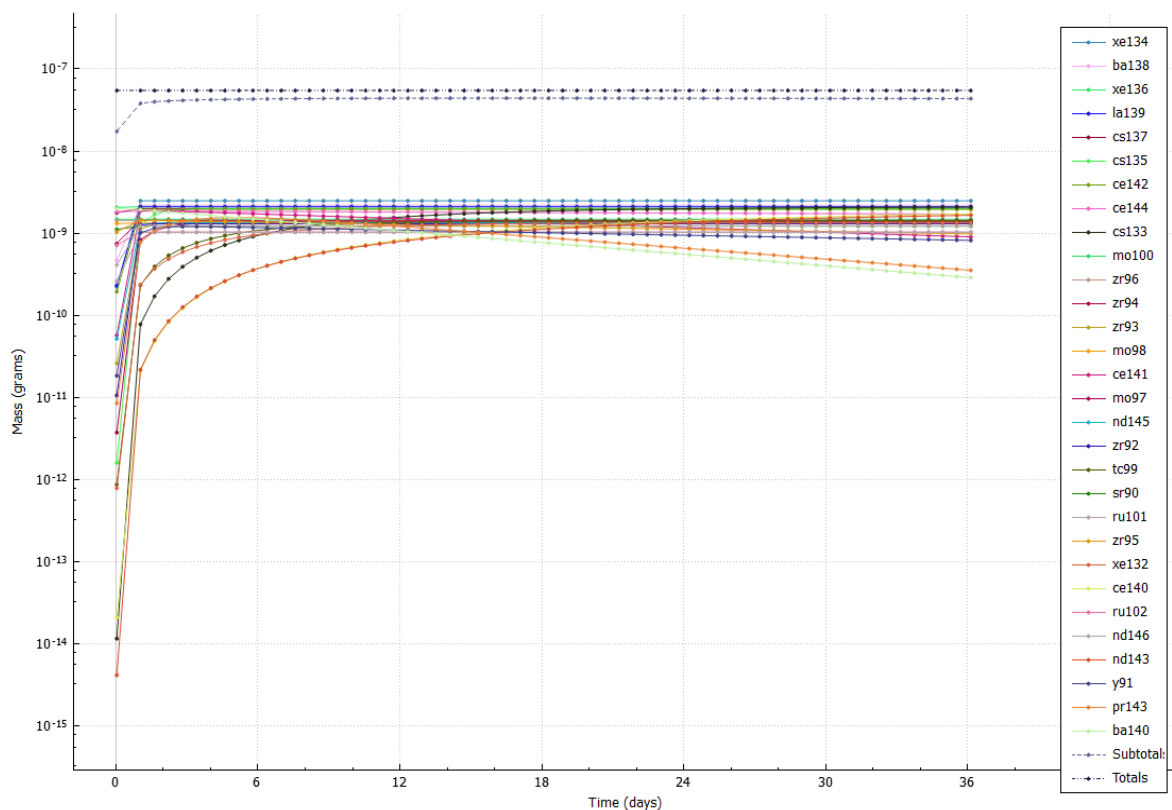


Figure 43. An ORIGIN-generated plot of fission product masses over the course of a 36-day decay after the irradiation of 80 μg ^{235}U for 48.5 minutes²⁰⁹.

Table 22. Irradiation and decay details for each HEU target.

Target (date)	^{235}U mass (μg)	Irradiation time (fissions)	Decay time before leach (days)	Decay time before analysis (days)
Target 1 (August 2017)	30	50 min ($\sim 5\text{E}13$)	15	36.1
Target 2 (August 2017)	80	50 min ($\sim 1\text{E}14$)	15	36.1
Target 3 (September 2018)	80	60 min ($\sim 1\text{E}14$)	6	7.5

Table 23. Irradiation parameters used for ORIGEN models.

Variable	Target 1 values	Target 2 values	Target 3 values
Irradiation time	50 min	50 min	60 min
Flux (from monitors)	6.69E14 n·(cm-s) ⁻¹ ²³⁵ U = 35.0E-6	6.69E14 n·(cm-s) ⁻¹ ²³⁵ U = 80.0E-6	6.57E14 n·(cm-s) ⁻¹ ²³⁵ U = 81.089E-6
Material (g)	²³⁸ U = 2.163E-6 ²³⁴ U = 3.829E-7	²³⁸ U = 4.944E-6 ²³⁴ U = 8.752E-7	²³⁸ U = 5.019E-6 ²³⁴ U = 8.91E-7
Decay time	36.1 days	36.1 days	178, 504, 1018 h

6.3.3 HEU Post-Irradiation and RAPID Analysis

After irradiation, several days needed to pass before leaching occurred (for the radioactivity to decrease to a limit that the building could handle): to leach, the ampoule was submerged in 4M HNO₃ (1 mL) and crushed with a mini-vice in the hood (Figure 44). Once crushed, the solution and glass were transferred to a Savillex container with an additional 2 mL nitric (total of 3mL), sealed, and heated for 4 h at ~90°C; after 4 h, the hot plate was turned off, but the container stayed closed on the plate overnight to ensure a thorough leach. The general process for each ampoule post-irradiation is displayed in Figure 44, along with accompanying illustrations.

Mass bias measurements were made using natural standards with every analysis to correct for the daily fluctuation of ICPMS sensitivity, which (along with the element and its elution time from the HPIC) drives the precision, bias, and detection limit of RAPID. Generally, each sample is bracketed by a standard to measure the mass bias and to observe any changes that occurred after sample injection/analysis.

6.3.3.1 Targets 1 & 2

For Targets 1 & 2 (which were irradiated at the same time in the same rabbit), the cooling period was 15 days after irradiation before crushing and leaching was performed. To verify complete

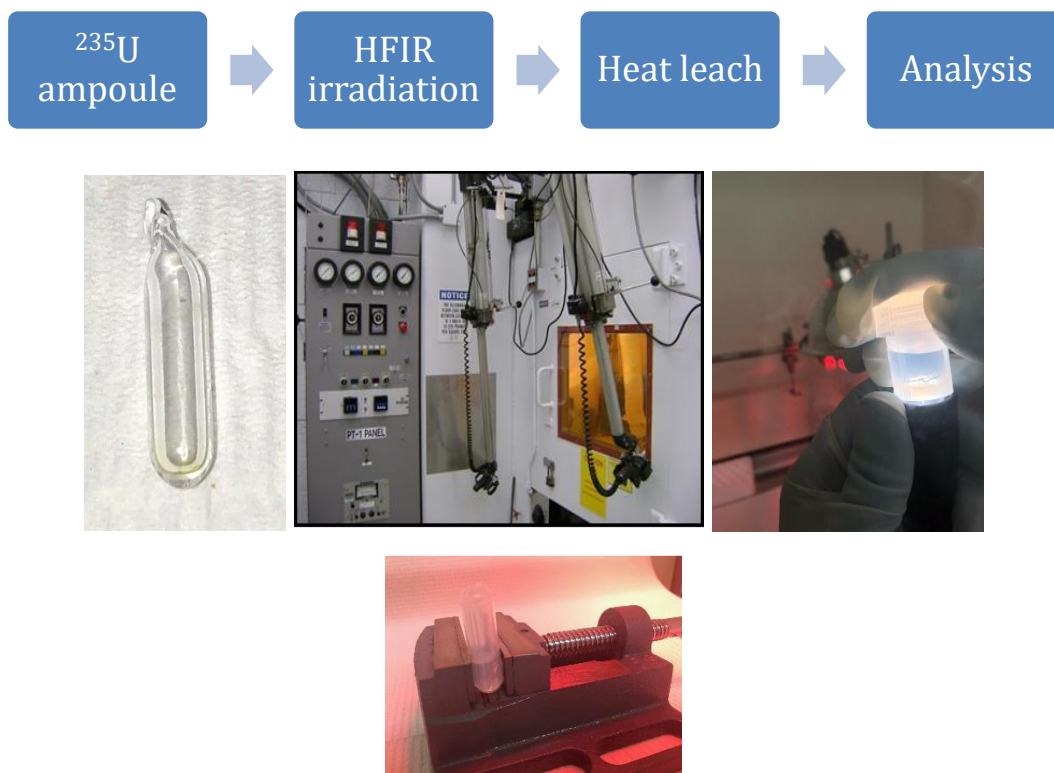


Figure 44. Top: major sample process steps; middle: correlating photos to the process (ampoule, irradiation station, glass in leach); bottom: mini-vice used to crush ampoule.

sample dissolution, the ^{235}U content was determined for each leached target using offline ICPMS and external calibration.

Next, at 36 days post-irradiation, the fission-produced lanthanides, ruthenium, strontium, and cesium were analyzed with RAPID (using 52-min elution profile given in Table 10) and compared with the ORIGEN mass predictions, which ranged in the high-femtogram/low-picogram range. As these masses are very close to the RAPID detection limits, any contamination, systematic or background, of the sample may interfere with these measurements. This effect may be negated by calculation of the natural isotopic abundance vs. fission isotopic abundance and the subsequent subtraction of the predicted natural quantities. For this analysis, the focus was on isotopic ratios of

the HEU fission products rather than the mass itself and comparison to the ORIGEN predictions due to the natural contamination interference.

6.3.3.2 Target 3

For Target 3, the goal was timeliness and multiple analyses over time to observe the slight isotopic shifts of some of the fission products (e.g. neodymium, promethium, samarium) as one decayed into the next, in addition to comparison with ORIGEN mass predictions. Once the sample was crushed and leached, it was analyzed several times over the course of the following six weeks (using 52-min elution profile given in Table 10) – the timeline is detailed in Table 24. The sample receipt and analysis timeline for this target was much shorter than for Targets 1 & 2 (see Table 23) to better observe these fission products shifts, as they happened on a short-medium lived decay timeframe. Additionally, analyzing these short-medium lived fission products sooner provided more mass to analyze with RAPID, allowing for observation of fission products in Target 3 that were not observed in Targets 1 or 2 (e.g. ^{149}Pm , $t_{1/2} = 53 \text{ h}$).

In addition to the RAPID measurements of the sample, an accompanying HPGe analysis was performed to obtain supplementary data to validate the ICPMS data as well as acquire measurements of radioactive fission products beyond the detection limits of RAPID. Once the HPGe and RAPID measurements were completed, the resulting fission product masses and isotopic ratios were compared to that predicted by ORIGEN, thus calculating recovery of the fission products from the irradiated silica ampoule. Other additional analyses included offline ICPMS for first, the uranium (measured with IDMS) and secondly, the fission products.

The resulting irradiated HEU solution was also used to create ORNL surrogate debris (as described in section 1.4.1); the solution was combined with the zeolite before going through the plasma torch. NACIL was given samples of this product before and after going through the torch so the potential

Table 24. Target 3 timeline from irradiation to analyses with both HPGe and RAPID.

Process		HPGe	RAPID
Irradiation	9/25/2018	-	-
Leach	10/1/2018	-	-
U IDMS	10/2/2018	-	-
FP analysis 1	-	10/3/2018	10/2/2018
Offline ICPMS	10/8/2018	-	-
FP analysis 2	-	10/15/2018	10/16/2018
FP analysis 3	-	10/22/2018	11/6/2018

isotopic fractionation could be observed. However, due to plasma torch complications, no attainable results were produced and as such, will not be covered in this dissertation.

6.4 Results and Discussion

6.4.1 Material Analyses

Using external calibration, the lanthanide contamination in the starting uranium material was calculated, given in Table 25. The error was calculated by the standard deviation (given in Qtegra) of the peak areas between the triplicate injections and applied to the final concentrations. In order to verify that these were naturally abundant lanthanides, various isotopic ratios were calculated and compared to that of a natural standard. As can be seen in Table 25, all the ratios are close to 100% of natural, verifying that this contamination is indeed natural. Notably, since these exist at such low concentrations, the peak shapes are not always ideal (i.e. Gaussian), which then affects the accuracy of the measurement, seen by the large error in cerium.

During this experiment, it was discovered that the nitric acid concentration of the samples affects the retention times of the lanthanides; generally, analyses are done with 2% nitric acid (~0.4M). Over the course of this project, analyses were conducted using concentrations ranging from 0.4M to 2M in a uranium matrix. The varying retention times can be seen in Figure 45. One of the samples used to demonstrate this retention time shift was one of the irradiated HEU samples, thus

the existence of promethium (which does not occur naturally). During the peak selection process in Qtegra, a user-specified time window is given to find a peak (i.e. a window of 30 s looks for any peak within that the elution time ± 30 s), which automatically builds in an inherent uncertainty (or standard deviation). Considering this window in tandem with the elution times, all times fall within two times that standard deviation (approximately 3.5% RSD), no matter the acid concentration. All other parameters were kept the same for each of these runs, though the other main variable is the pH of the eluents, which potentially varies at an undetermined rate as a function of the ammonium hydroxide evaporating out of the solution and dissolution of CO_2 into the eluents neutralizing the OH^- . Since these analyses were performed at different times (not sequentially within the same week), the freshness of the eluents was the main variable other than the acid concentration. Life of the column also needs to be considered, as a well-used column will not function the exact same as a fresh column due to conditions such as degradation of the resin.

Obviously, these shifts do not affect the measurement of each lanthanide, as they still elute sequentially, but it can make an analysis more difficult if the standards and samples have different elution times. The main drawback for future analyses with this elution variability is the ability to accurately fraction collect based off predicted elution times. Matrix matching (acid concentration) the standards and samples helps the elution times stay consistent between runs, but the overall stability of the elution times from day to day operations is ideal.

Table 25. HEU standard U930-D lanthanide concentrations pre-irradiation.

Isotope	Conc. (ppt)	+/-	Ratio		Recovery of natural
¹⁴⁰ Ce	19.41	5.978	140/142	8.015	101%
¹⁴¹ Pr	8.59	0.217	-	-	-
¹⁴² Ce	1.82	0.269	-	-	-
¹⁴⁴ Nd	2.54	0.249	144/146	1.389	100%
¹⁴⁶ Nd	2.17	0.292			
¹⁵² Sm	0.45	0.026	147/152	0.568	101%
¹⁵³ Eu	0.27	0.052	151/153	0.927	101%
¹⁵⁷ Gd	0.63	0.270	157/158	0.63	99%

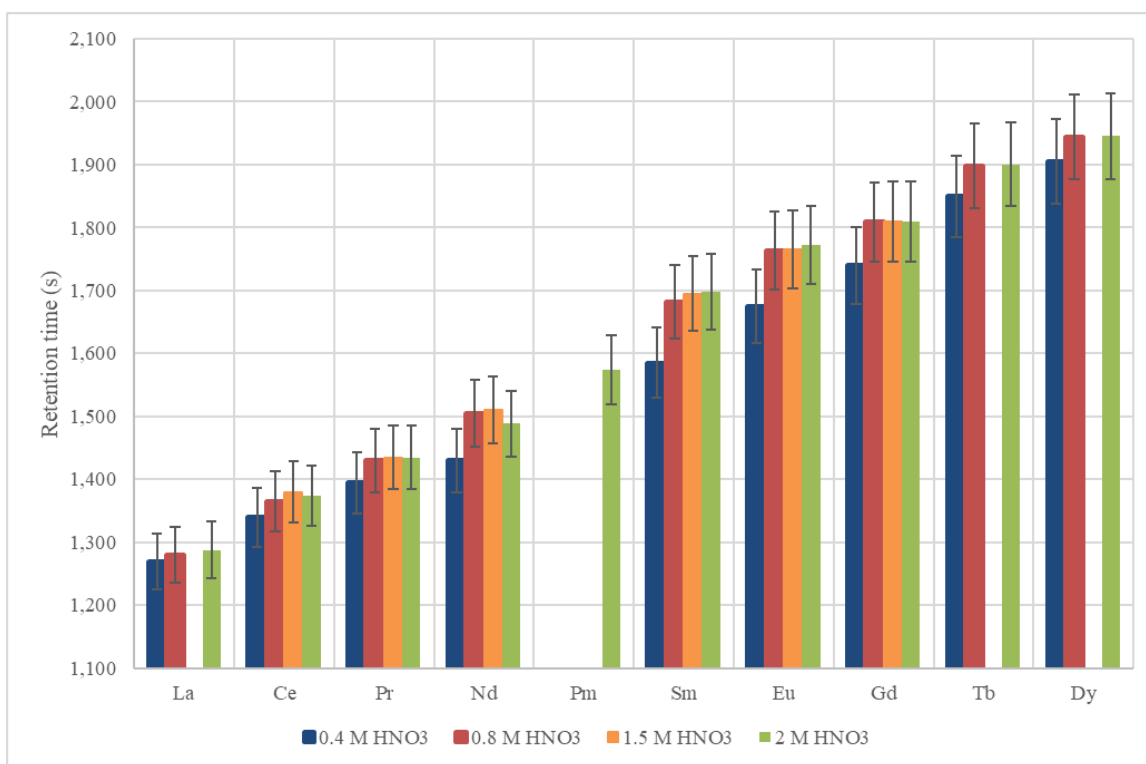


Figure 45. Varying retention times of the lanthanides in four different concentrations of nitric acid.

6.4.2 Analysis of Targets 1 & 2

The results of Targets 1 & 2 and subsequent comparison to ORIGEN predictions are published in JRNC (see section 6.1): published data are summarized in this section, and additional information is presented in more detail.

The ^{235}U masses for Targets 1 & 2, determined by offline ICPMS, were 27.4 ± 2.7 and 77.0 ± 7.7 μg total, respectively, which correlates with the original calculations from the HPGe measurements of 30 ± 3.5 and 80 ± 5 μg (see section 4.3.4.1). The expected fission product distributions, as calculated by ORIGEN with the updated mass data, are illustrated in Figure 46 for each target, given an irradiation time of 48.5 minutes and a decay of 36.1 days, and show how much fission product mass was generated. To generate these fission product curves, the ORIGEN-predicted masses of all isobars (e.g. ^{140}La , ^{140}Ba , ^{140}Ce) were summed, and thus the “two hump” fission product curves were generated for each specific target.

Next, the analyses of various fission products (strontium, ruthenium, cesium, cerium, neodymium, and samarium) compared with ORIGEN estimates will be presented. Since each of the targets was analyzed only once with RAPID, instead of the usual triplicate analysis, no precision data is available to base uncertainty values on, thus this study was performed as a proof of concept for comparison of ORIGEN-predicted values to measured values with RAPID. Most comparisons are given in terms of isotopic ratios due to the natural contamination that existed in these samples. Each of these elements was separated from its isobaric interference(s), as documented in the JRNC publication²⁰⁸.

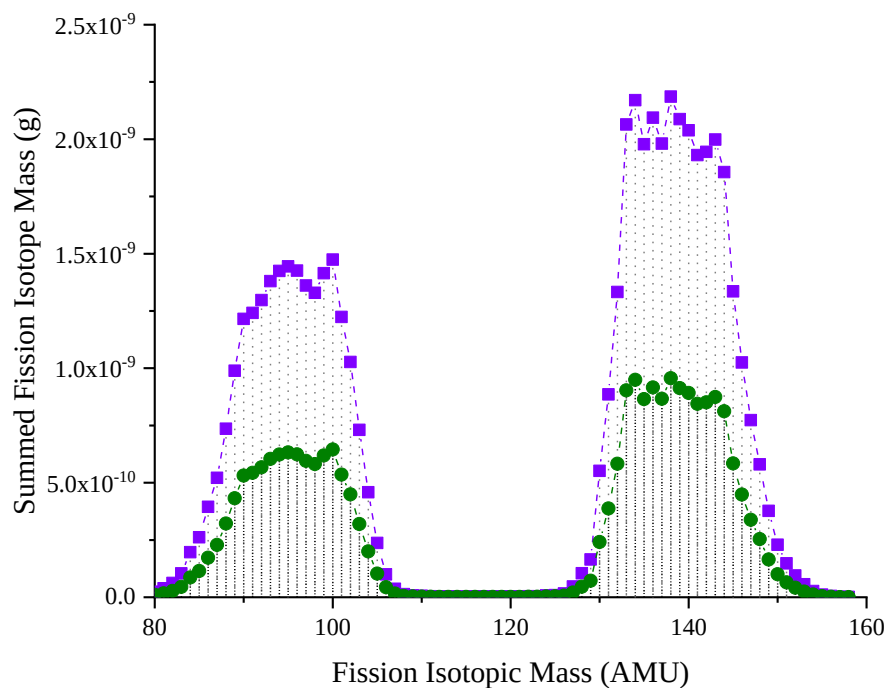


Figure 46. ORIGIN-calculated fission product distributions for Target 1 (green circles) and Target 2 (purple squares) after an irradiation time of 48.5 minutes, where all isobars were summed²⁰⁸.

First, strontium (masses 89 and 90, $t \sim 800$ s) was separated from its interferences, yttrium (m/z 89, $t \sim 2000$ s) and zirconium (m/z 90, $t \sim 2300$ s). The total mass injected on the column was close to the system's detection limits (i.e. 5 pg of ^{89}Sr for Target 2), and the isotopic ratio measured was $^{89}\text{Sr}:^{90}\text{Sr}$. However, even with this low-level injection, the recovery of this ratio compared to predicted was 93% for both targets (0.46 vs 0.49 as calculated by ORIGIN); uncorrected mass bias effects may be the reason that the recovery is not closer to 100%, as the bias effects are more noticeable in the lower mass range. A natural low-level strontium standard could possibly be used to address this next time, utilizing the ratio $^{86}\text{Sr}:^{87}\text{Sr}$.

Next, ruthenium's isotopic ratio was $^{101}\text{Ru}:^{102}\text{Ru}$, which was injected again at the isotopic LODs (4 pg injection for Target 1) and demonstrated RAPID's sensitivity. The measured ratios of 1.05

and 1.20 resulted in recoveries of 85% and 101%, respectively for Targets 1 and 2, compared to an ORIGEN-predicted 1.19. The ruthenium peaks measured in Target 1 were barely above background ($\sim 5\times$), which most likely accounts for the low recovery compared to ORIGEN.

The next element analyzed, cesium, appeared to have natural contamination (which was not measured in the uranium blank measurement), which affected the analysis of the fission-produced cesium in the targets. This contamination was calculated to be $\sim 15\%$ and 2% (targets 1 and 2 respectively), through comparison of measured isotopic composition and ORIGEN-predicted composition, assuming natural contamination. Since the natural contamination is purely ^{133}Cs , and the fission-produced isotopes include ^{135}Cs and ^{137}Cs , these two isotopes can still be measured and compared with ORIGEN values. If these were analyzed with traditional methods, gamma spectroscopy could measure ^{137}Cs but not ^{135}Cs (due to its long half-life), and offline ICPMS would not be able to distinguish between cesium and barium (^{135}Ba , 6.6% natural abundance, ^{137}Ba , 11.2% natural abundance). RAPID, however, separated cesium ($t \sim 230$ s) and barium ($t \sim 90$, 275 s) even with the naturally-occurring barium concentration existing at a level 3–4x the cesium concentration in the samples and obtained recoveries near 100% for both targets (see Table 27) compared with ORIGEN.

Next, cerium, neodymium, and samarium were analyzed and compared to ORIGEN; Figure 47 demonstrates the degree of separation obtained with the RAPID method for this sample, with an inset labeling each lanthanide and its elution time. Each of the lanthanides selected for this analysis (Ce, Nd, Sm) were separated from corresponding isobaric interferences. Additionally, lanthanum oxide (m/z 155) and cerium oxide (m/z 156) can both be observed in this illustration showing separation from any gadolinium in the sample (for these samples, the mass of gadolinium injected was below RAPID's detection limit).

Table 26. Measured cesium isotopic abundances for both targets compared with the predicted ORIGEN ratio at 36.1 days decay post-irradiation²⁰⁸.

Target	¹³³ Cs atom (%)	¹³⁵ Cs atom (%)	¹³⁷ Cs atom (%)	¹³⁵ Cs: ¹³⁷ Cs ORIGEN	¹³⁵ Cs: ¹³⁷ Cs measured	% Recovery
1	43.2	28.7	28.2	0.999	1.018	102
2	33.1	33.5	33.9	0.999	0.987	99

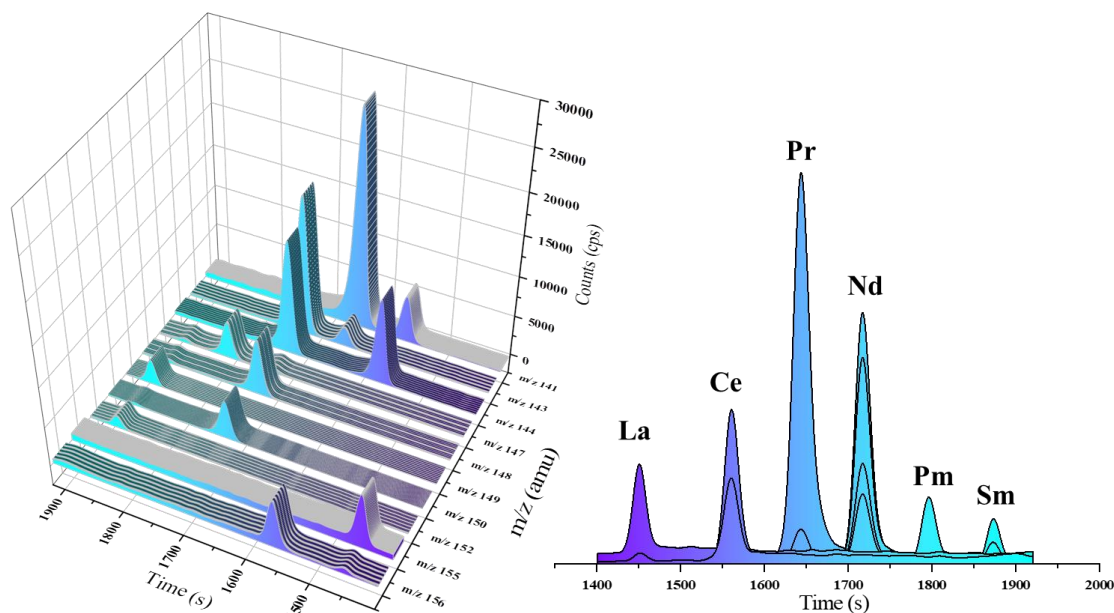


Figure 47. A 3-D chromatogram of m/z ranging from 141-156 illustrating separation between lanthanides. Inset: a 2D cut of the chromatogram with labels and elution times of all pertinent lanthanides²⁰⁸.

As given earlier in Table 25, the natural contamination of cerium in the stock uranium solution was non-zero, and it was noticeable in RAPID's analysis (in addition to any other natural contamination added during the sample preparation). However, fission-produced isotopes 141 ($t_{1/2} = 32.5$ d) and 144 ($t_{1/2} = 285$ d) were measurable (though an order of magnitude lower than the natural isotopes 140 and 142) and compared with ORIGEN. As seen in Figure 47, good separation was produced in the 141 and 144 m/z traces from their interferences (¹⁴¹Pr and ¹⁴⁴Nd) in addition to the 143 trace for elemental confirmation of both the neodymium and

praseodymium. The ORIGEN comparisons are given in Table 27 for both targets, showing nearly 100% recovery from the ORIGEN predictions.

The next lanthanide analyzed, neodymium, also existed as natural contamination in the starting uranium; it was observed that the composition measured in the irradiated sample was neither natural nor fission but rather a mixture of both. ^{147}Nd is the only non-natural isotope, and ^{142}Nd is the only non-fission produced isotope, so this knowledge was used to compare natural isotopic composition to ORIGEN (fission isotopic composition), then the natural contribution must be subtracted from the final RAPID measurements. Using these variables, the contribution from natural and fission can be calculated in the resulting data, as seen in Table 28. The natural contribution was approximately 65%, while the fission contribution was 35% (taken as an average between the two targets). Using this information, the average fission-generated atom percent of each neodymium isotope was corrected to compare with ORIGEN (values listed for fission abundance in Table 28). As can be seen, the values match within the 2σ uncertainty of the measurement.

The final element analyzed in this experiment was samarium, which also had natural contamination. However, the concentration of samarium in the original solution was low-level, thus additional contamination of the targets (particularly Target 1) must have occurred during preparation. During analysis, it was found that there was more natural contamination in Target 1

Table 27. Measured vs. ORIGEN-predicted cerium ratios in both targets using a 36.1 day decay time²⁰⁸.

Target	Observed $^{141}\text{Ce}:^{144}\text{Ce}$	Calculated $^{141}\text{Ce}:^{144}\text{Ce}$	$^{141}\text{Ce}:^{144}\text{Ce}$ % recovery
1	0.516	0.528	98
2	0.523	0.528	99

Table 28. Measured neodymium atom percent abundances of each isotope as compared to naturally-occurring and ORIGEN-generated fission-induced abundances. The average, corrected fission abundances of the targets is calculated²⁰⁸.

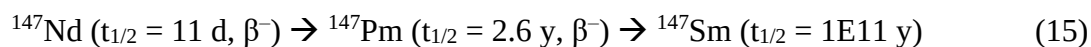
Isotope	Natural abundance (atom %)	Fission Abundance (atom %, calc.)	Target 1 (atom %, meas.)	Target 2 (atom %, meas.)	Average fission atom % (corr.) (2 σ)
¹⁴² Nd	27.15	0.00	18.0	17.8	0.0
¹⁴³ Nd	12.17	33.08	20.0	20.1	33.2(1)
¹⁴⁴ Nd	23.80	3.11	16.1	15.9	3.0(1)
¹⁴⁵ Nd	8.29	26.45	14.6	15.0	26.3(8)
¹⁴⁶ Nd	17.19	20.16	17.6	18.3	19.5(17)
¹⁴⁷ Nd	0.00	1.55	0.6	0.5	1.6(2)
¹⁴⁸ Nd	5.76	11.26	8.0	7.5	11.7(14)
¹⁵⁰ Nd	5.64	4.39	5.0	4.8	4.7(7)

than in Target 2, which negated the usefulness of its isotopic data; however, Target 2 data was still usable. Unfortunately, ¹⁵³Sm ($t_{1/2} = 46$ h) had already decayed away by the time the analysis was performed, leaving only one non-natural isotope, ¹⁵¹Sm ($t_{1/2} = 90$ y), which was observed in conjunction with ¹⁴⁹Sm to compare with ORIGEN. This ratio was recovered at 99%, and clear separation was obtained between ¹⁵¹Sm ($t = 1875$ s) and its main isobar, ¹⁵¹Eu ($t = 1915$ s, which also varied in level of contamination).

Lastly, and most noteworthy, is the separation obtained between the ¹⁴⁷Nd, ¹⁴⁷Pm, and ¹⁴⁷Sm peaks (see Figure 48) – this can only be obtained through an effective separation and MS measurement. The ratio of ¹⁴⁷Nd:¹⁴⁷Pm was compared to that of ORIGEN, and recoveries of 97.0% and 99.5% were calculated for Target 1 and 2, respectively. This is notable, given that the injected masses of ¹⁴⁷Nd on the column were merely 200 fg and 600 fg, respectively.

Equation 15 presents the decay chain of these isobars; there are gammas emitted by ¹⁴⁷Nd and ¹⁴⁷Pm as they decay, however, the latter is very weak (0.00285% intensity), and traditional

radiochemical techniques may struggle with quantifying these emissions in real-world samples. Conversely, with RAPID and a semi-quantitative analysis using a ^{147}Sm standard, concentration measurements of high-femtogram level ^{147}Pm should be possible with 5–10% uncertainty. Previous work has determined that the lanthanide response using RAPID is very consistent (only a 5% increase in signal from ^{159}Tb vs. ^{139}La), and thus the response of ^{147}Sm should be adequate to semi-quantify ^{147}Pm . That information, plus the good recovery shown for the ^{147}Nd : ^{147}Pm compared to ORIGEN, demonstrate the promethium does not demonstrate from that trend. Additionally, samarium and promethium have similar first ionization potentials (5.643 eV and 5.582 eV respectively ²¹¹), which indicates similar response as the sample is ionized in the ICPMS.



To summarize this study, Table 29 lists the final ratio recoveries with respect to ORIGEN for each of the targets, illustrating RAPID’s capability to analyze low-level fission products to within 1% of ORIGEN’s predicted ratios. Target 2 was 2.3x larger than Target 1, and that difference can be seen in the accuracies of the ratios. Furthermore, the precision and sensitivity of RAPID for these samples did not appear to be affected by the uranium matrix, and these analyses were performed in less than an hour each.

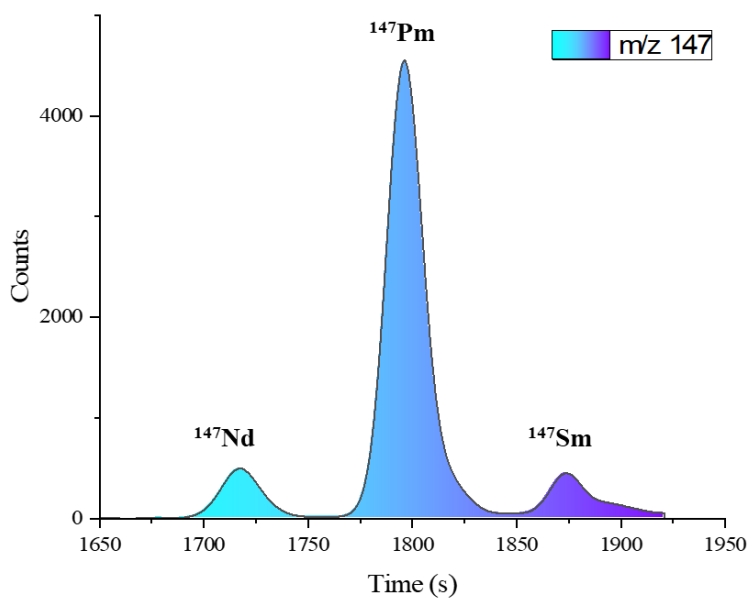


Figure 48. Chromatogram of the 147 m/z trace for Target 2 illustrating separation between neodymium, promethium, and samarium.

Table 29. Summary of the isotopic ratio recoveries compared to ORIGEN for Targets 1 and 2²⁰⁸.

Element	ORIGEN-calculated ratio	Measured ratio in Target 1 (% recovery)	Measured ratio in Target 2 (% recovery)
¹³⁵ Cs: ¹³⁷ Cs	0.999	1.018 (102)	0.987 (99)
⁸⁹ Sr: ⁹⁰ Sr	0.49	N/A	0.46 (93)
¹⁰¹ Ru: ¹⁰² Ru	1.19	1.05 (85)	1.20 (101)
¹⁴¹ Ce: ¹⁴⁴ Ce	0.528	0.516 (98)	0.523 (99)
¹⁴⁷ Nd: ¹⁴⁷ Pm	0.116	0.112 (97)	0.115 (100)
¹⁴⁹ Sm: ¹⁵¹ Sm	2.55	N/A	2.53 (99)

6.4.3 Analysis of Target 3

These results were published in Talanta (see section 6.2) and will be summarized and supplemented accordingly.

The next irradiated HEU study was performed in September 2018 when Target 3 was prepared and irradiated per the conditions given in section 6.3.3.2. Following the timeline also outlined in that section, the leach was completed shortly after irradiation, then the first set of measurements: offline ICPMS for uranium content, and RAPID/HPGe for various fission products. Quantification of the uranium from the leach with IDMS resulted in a total mass of 86.66 +/- 0.46 µg – this corresponds to ~80 µg ^{235}U , which was the target ^{235}U mass. Table 30 below gives the results from the first RAPID measurement as a function of isotopic mass this time instead of only isotopic ratios, and Table 31 gives the first round of HPGe data. Highlighted are the isotopes measured with both techniques (**red text**, asterisk) and gamma-emitting isotopes measured with RAPID instead of HPGe (**black text**, asterisk). The recoveries of the RAPID vs. HPGe measurements for these common isotopes range from 98%–106%. The average precision of these measurements is ~2%; however, in operational practice, NACIL generally reports conservative uncertainties of 10% (which is reported in Table 30).

As can be seen in Table 30, the average recovery of the fission products in the leachate compared with ORIGEN mass predictions is ~60% for both the HPGe and RAPID data sets. Notably, the recovery of ^{239}Np from the HPGe data is near 100% (as was the uranium recovery). It is hypothesized that the energy of the fission products (200 MeV released per fission event) propelled them into the quartz walls of the ampoule. To test the legitimacy of this hypothesis, SRIM was used to calculate the range of fission products with 200 MeV into a silicon material. These calculations projected that the resulting fission products embed themselves ~20–25 µm into the

Table 30. RAPID-generated results from 10/2/2019 comparing calculated mass measured to ORIGEN-predicted mass.

Isotope	ng total in target	Error (10%)	ORIGEN-predicted mass (ng)	Recovery	Isotopic mass analyzed (pg)
⁸⁹ Sr	4.84E-01	4.84E-02	1.07E+00	45%	4.03
⁹⁰ Sr*	6.78E-01	6.78E-02	1.45E+00	47%	5.65
⁸⁹ Y	5.70E-02	5.70E-03	1.14E-01	50%	0.47
⁹¹ Y*	6.78E-01	6.78E-02	1.37E+00	50%	5.65
¹⁰¹ Ru	6.20E-01	6.20E-02	1.46E+00	42%	5.17
¹⁰² Ru	5.15E-01	5.15E-02	1.23E+00	42%	4.29
¹⁰⁴ Ru	3.36E-01	3.36E-02	5.47E-01	61%	2.80
¹³³ Cs	3.68E-01	3.68E-02	1.36E+00	27%	3.07
¹³⁵ Cs*	9.10E-01	9.10E-02	2.34E+00	39%	7.59
¹³⁷ Cs*	1.34E+00	1.34E-01	2.37E+00	56%	11.15
¹³⁹ La	1.48E+00	1.48E-01	2.49E+00	59%	12.32
¹⁴⁰ La*	1.36E-01	1.36E-02	2.29E-01	59%	1.13
¹⁴⁰ Ce	3.45E-01	3.45E-02	5.82E-01	59%	2.87
¹⁴¹ Ce*	1.03E+00	1.03E-01	1.98E+00	52%	8.57
¹⁴² Ce	1.35E+00	1.35E-01	2.32E+00	58%	11.22
¹⁴³ Ce*	3.15E-02	3.15E-03	5.68E-02	55%	0.26
¹⁴⁴ Ce*	1.25E+00	1.25E-01	2.18E+00	57%	10.42
¹⁴¹ Pr	1.73E-01	1.73E-02	3.27E-01	53%	1.44
¹⁴³ Pr*	9.42E-01	9.42E-02	1.76E+00	54%	7.85
¹⁴³ Nd	3.24E-01	3.24E-02	5.75E-01	56%	2.70
¹⁴⁴ Nd	2.67E-02	2.67E-03	3.97E-02	67%	0.22
¹⁴⁵ Nd	9.62E-01	9.62E-02	1.60E+00	60%	8.01
¹⁴⁶ Nd	7.56E-01	7.56E-02	1.22E+00	62%	6.30
¹⁴⁷ Nd*	3.45E-01	3.45E-02	5.78E-01	60%	2.87
¹⁴⁸ Nd	4.30E-01	4.30E-02	6.93E-01	62%	3.58
¹⁵⁰ Nd	1.80E-01	1.80E-02	2.74E-01	66%	1.50
¹⁴⁷ Pm*	2.09E-01	2.09E-02	3.45E-01	61%	1.74
¹⁴⁹ Pm*	2.65E-02	2.65E-03	4.53E-02	58%	0.22
¹⁴⁹ Sm	2.34E-01	2.34E-02	4.05E-01	58%	1.95
¹⁵¹ Sm*	9.96E-02	9.96E-03	1.75E-01	57%	0.83
¹⁵² Sm	7.71E-02	7.71E-03	1.13E-01	68%	0.64
¹⁵³ Sm	2.82E-03	5.64E-04	4.74E-03	59%	0.02
¹⁵⁴ Sm	2.32E-02	2.32E-03	3.21E-02	72%	0.19

Table 31. HPGe measurement from 10/03/2018 compared with ORIGEN data.

Isotope	Activity total (Bq)	Uncertainty	Specific act. (Bg/g)	Mass (ng)	ORIGEN-predicted mass (ng)	Recovery
⁹⁵ Nb	8.97E+04	3.82E+03	1.4548E+15	6.17E-02	1.32E-01	47%
⁹⁵ Zr	6.33E+05	1.96E+04	7.9499E+14	7.96E-01	1.58E+00	50%
⁹⁷ Nb	2.31E+04	2.07E+03	9.959E+17	2.32E-05	4.18E-05	56%
⁹⁷ Zr	2.08E+04	1.95E+03	7.1457E+16	2.91E-04	5.40E-04	54%
⁹⁹ Mo	1.68E+06	5.86E+04	1.778E+16	9.45E-02	2.21E-01	43%
^{99m} Tc	1.99E+06	1.91E+05	-	-	-	-
¹⁰³ Ru	4.16E+05	1.56E+00	1.196E+15	3.48E-01	7.58E-01	46%
¹⁰⁵ Rh	4.63E+04	1.49E+04	3.127E+16	1.48E-03	7.31E-03	20%
¹²⁷ Sb	5.95E+04	7.44E+03	9.9E+15	6.01E-03	1.32E-02	46%
¹³¹ I	6.11E+05	1.99E+04	4.5988E+15	1.33E-01	5.42E-01	25%
¹³² I	1.33E+06	2.86E+04	3.83E+17	3.47E-03	8.53E-03	41%
¹³² Te	1.46E+06	3.93E+04	1.143E+16	1.28E-01	2.77E-01	46%
¹³³ I	2.95E+04	1.05E+04	4.2E+16	7.02E-04	4.07E-03	17%
¹⁴⁰ Ba	2.17E+06	4.49E+04	2.7079E+15	8.01E-01	1.57E+00	51%
¹⁴⁰ La*	2.20E+06	3.56E+04	2.05722E+16	1.07E-01	2.25E-01	48%
¹⁴¹ Ce*	1.13E+06	4.30E+04	1.0547E+15	1.07E+00	1.95E+00	55%
¹⁴³ Ce*	4.93E+05	1.56E+04	2.45578E+16	2.01E-02	4.15E-02	48%
¹⁴⁴ Ce*	1.94E+05	2.98E+04	1.1783E+14	1.65E+00	2.17E+00	76%
¹⁴⁷ Nd*	1.01E+06	5.15E+04	2.994E+15	3.37E-01	5.56E-01	61%
¹⁴⁹ Pm*	3.44E+05	5.72E+04	1.467E+16	2.34E-02	3.73E-02	63%
²³⁹ Np	6.27E+04	6.57E+03	8.577E+15	7.31E-03	7.23E-03	101%

ampoule material during irradiation, which makes the leaching process non-trivial. Additional nitric acid (concentration of 1M) was added to the crushed ampoule and left to leach over the course of several weeks to assess what fission products were still embedded in the ampoule after the first leach. Data from this leach is presented in Table 32, obtained from an offline ICPMS measurement (and a RAPID screen for the ¹³⁷Cs), with precision-dictated standard deviation. Given that the recovery is ~15%, it can be assumed that there are still fission products remaining in the ampoule that can only be recovered with a more aggressive leaching process (i.e. microwave dissolution).

Another notable result is the discrepancy in the ^{133}Cs and ^{135}Cs recoveries, outliers even compared to the nominal 60% recoveries of the other fission products. Due to the fact that these isotopes are the daughters of ^{133}Xe and ^{135}Xe , respectively, any breach of the ampoule (and thus loss of the xenon gases) would have affected these masses. It was hypothesized that when the irradiation vessel returned to the lab at 24 h post-irradiation, a micro-fracture was created and the xenon lost from the sample. To verify this claim, the ORIGEN model was changed to simulate the loss of xenon at the 24 h mark and the final cesium masses adjusted accordingly. Table 33 gives the results from this updated model compared to the initial RAPID measurements in terms of both mass produced and isotopic atom percent; the predicted recoveries and similar atom percents support the hypothesis of xenon loss at that time.

Figure 49 illustrates the excellent elemental separation obtained for the lanthanides (cesium/barium, strontium, and yttrium are presented in the publication) with RAPID for this irradiated HEU sample at 178 h (~7.5 d) post-irradiation. For this analysis, masses injected on the column for each isotope ranged from 20 fg–10 pg, highlighting the low-level analytical capability of this method. Figure 49 gives the full 3D chromatogram (time vs. m/z vs. intensity) as well as a 2D chromatogram that better show the elemental separation (time vs. intensity). All elements of interest were separated from their isobaric interferences.

Table 32. Secondary leach measurement performed by offline ICPMS on 10/24/2018.

Isotope	Recovery from ORIGEN	2 σ
^{133}Cs	21.0%	0.4%
^{137}Cs	14.7%	0.4%
^{142}Ce	33.0%	0.3%
^{145}Nd	15.3%	0.3%
^{146}Nd	14.7%	0.7%
^{149}Sm	15.8%	2.5%

Table 33. 10/2/2018 cesium isotopic data compared to ORIGEN, assuming xenon loss at 24 h post-irradiation.

Isotope	RAPID (ng)	ORIGEN (ng)	Recovery	RAPID atom %	2 σ error	ORIGEN atom %
^{133}Cs	0.368	0.6405	58%	14.84	0.19	13.98
^{135}Cs	0.910	1.6635	55%	35.50	0.65	35.77
^{137}Cs	1.340	2.3701	56%	49.67	0.83	50.22

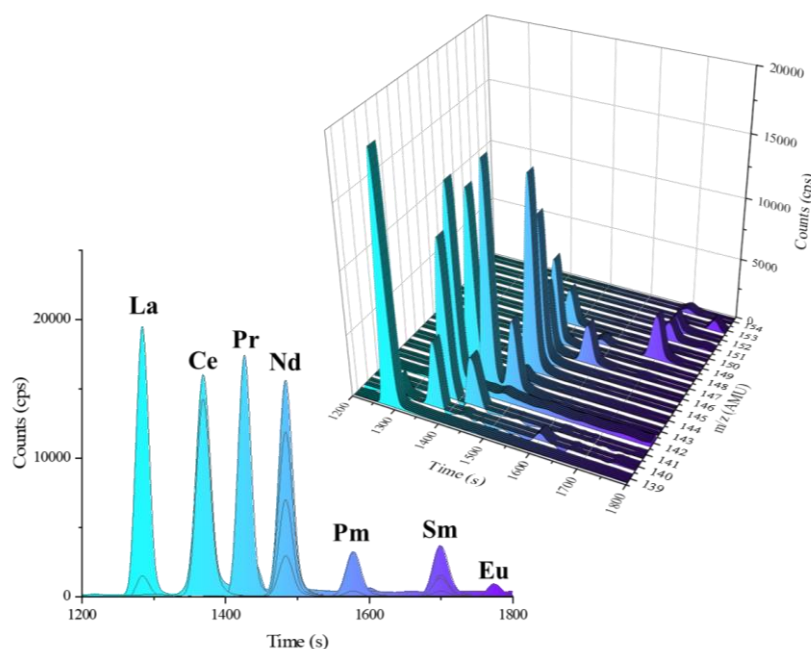


Figure 49. Elemental separation of the lanthanides, m/z 139–154, with elution time ranging from 1200–1800 s^{212} .

Over the course of the following six weeks, additional analyses were completed, both by RAPID and HPGe. Table 34 gives the RAPID results for each analysis, calculated in atom percent of each isotope, compared to the correlating ORIGEN-predicted atom percent. Due to the incomplete recovery of the fission products, atom percent was a more relevant characteristic to compare experimental data vs. modeled data. Each RAPID result is the average of a triplicate sample analysis, bracketed by natural standards to correct for the mass bias of the ICPMS. The masses of

these isotopes analyzed ranged from ~20 fg (e.g. ^{135}Sm) to ~10 pg (e.g. ^{145}Nd) with most of the highly-abundant isotopes showing a 1–3% precision and a 1–2% accuracy when compared with the ORIGEN predictions. To more accurately compare ^{133}Cs and ^{135}Cs measurements to ORIGEN, since the sample is no longer closed (and whatever xenon is generated will be immediately lost), the models were adjusted to lose all the xenon yet again when aliquots were pulled from the leach solution at 178 h post-irradiation. Given that the half-life of ^{133}I is 20.8 h, at 178 h, it will be close to its tenth cycle, which is generally when the rule of thumb is to assume it is now of negligible mass and will not contribute to its daughter's mass (^{133}Xe) any longer. Thus, it makes sense that the cesium isotopes will be constant mass and composition from this point onward from the standpoint of this short six-week study.

Performing multiple analyses over several weeks allowed for observation of ingrowth/decay of several fission products with shorter half-lives, particularly masses 143 (cerium, praseodymium, neodymium) and 147 (neodymium, promethium, samarium). Observable shifts in the $^{143}\text{Ce}/^{143}\text{Pr}/^{143}\text{Nd}$ and $^{147}\text{Nd}/^{147}\text{Pm}/^{147}\text{Sm}$ abundances were measured and the latter is illustrated in Figure 50. ^{143}Pr decays and decreases in intensity while ^{143}Nd increases as the daughter isotope in this decay; similarly, ^{147}Nd decays into ^{147}Pm . To confirm the accuracy of this data, the half-lives of both ^{147}Nd and ^{143}Pr were calculated by performing an exponential decay fit of the data in Excel, using the respective calculated masses of each isotope from each measurement (178, 504, 1018 h). The exponential decay equation is shown (Equations 16 & 17), where N and mass are interchangeable (i.e. mass is plotted as a function of time). Once the data was fit in Excel with an exponential function, the coefficient, equal to $(-\lambda \cdot t)$, was used to calculate each half-life. The resulting half-lives were calculated to be 10.6(3) d and 13.9(4) d, respectively, compared to $t_{1/2}^{147}\text{Nd} = 10.98 \text{ d}$, $t_{1/2}^{143}\text{Pr} = 13.57 \text{ d}$ ²¹³. Table 35 lists several isotopic ratios of neodymium that

Table 34. Measured atom % by RAPID compared to those calculated in ORIGEN over six weeks post-irradiation. ORIGEN cesium numbers, highlighted in red, are updated from the published paper²¹².

Time post-irradiation (h)	178		504		1018	
Isotope	RAPID (meas. at. %) (2 σ , n=3)	ORIGEN (at. %)	RAPID (meas. at. %) (2 σ , n=3)	ORIGEN (at. %)	RAPID (meas. at. %) (2 σ , n=3)	ORIGEN (at. %)
⁸⁸ Sr	26.5(3)	26.2	27.5(10)	27.7	29.3(9)	29.8
⁸⁹ Sr	31.1(2)	31.4	27.7(7)	27.5	21.5(3)	22.1
⁹⁰ Sr	42(2)	42.4	45(1)	44.8	49.1(6)	48.1
⁸⁹ Y	7.7(8)	7.9	20.5(7)	21.0	37.3(6)	37.1
⁹¹ Y	92.3(8)	92.1	79.5(7)	79.0	62.7(6)	62.9
¹³³ Cs	14.8(2)	14.0	14.5(3)	14.1	15.2(6)	14.1
¹³⁵ Cs	35.5(6)	35.8	34.6(14)	35.8	35(1)	35.8
¹³⁷ Cs	49.7(8)	50.2	50.9(15)	50.1	49.7(8)	50.1
¹³⁹ La	91.5(3)	91.6	95.68(5)	95.6	98.5(3)	98.6
¹⁴⁰ La	8.4(3)	8.4	4.32(5)	4.4	1.5(3)	1.4
¹⁴⁰ Ce	8.4(2)	8.2	20.1(17)	21.2	31.2(4)	29.4
¹⁴¹ Ce	26.2(5)	27.6	20.8(7)	19.8	12.6(4)	12.7
¹⁴² Ce	34(2)	32.2	31.6(4)	31.1	30.2(4)	31.3
¹⁴³ Ce	0.76(4)	0.8	0.07(3)	0.0	0(0)	0.0
¹⁴⁴ Ce	30.3(4)	29.8	27(1)	27.8	26.0(6)	26.6
¹⁴¹ Pr	15.4(4)	15.9	48(1)	48.9	82.3(6)	82.0
¹⁴³ Pr	84.6(4)	84.1	52(1)	51.1	17.7(6)	18.0
¹⁴³ Nd	10.9(3)	11.8	26.3(5)	27.0	33.7(4)	34.4
¹⁴⁴ Nd	0.92(14)	0.8	2.5(2)	2.0	3.5(2)	3.6
¹⁴⁵ Nd	32.6(4)	32.2	28.4(13)	28.4	26.4(5)	25.9
¹⁴⁶ Nd	25(1)	24.6	21.5(3)	21.6	19.8(3)	19.8
¹⁴⁷ Nd	11.3(2)	11.5	4.15(11)	4.2	1.0(1)	1.0
¹⁴⁸ Nd	13.6(5)	13.7	12.4(9)	12.1	11.3(2)	11.0
¹⁵⁰ Nd	5.6(4)	5.4	4.8(6)	4.7	43(2)	4.3
¹⁴⁷ Pm	88.7(5)	88.5	99.9(1)	99.9	100.0(1)	100.0
¹⁴⁹ Pm	11.3(5)	11.5	0.08(1)	0.1	0(0)	0.0
¹⁴⁷ Sm	0(0)	0.0	0.8(4)	0.8	2.7(1)	2.4
¹⁴⁹ Sm	54.6(6)	56.0	57(2)	58.2	56(2)	57.3
¹⁵¹ Sm	23(1)	23.8	22(2)	22.6	22.2(5)	22.2
¹⁵² Sm	17(1)	15.3	15(1)	14.4	14(1)	14.1
¹⁵³ Sm	0.62(7)	0.6	0.01(3)	0.0	0(0)	0.0
¹⁵⁴ Sm	4.5(6)	4.3	5(1)	4.0	4.9(4)	3.9

shifted during the three analyses and the ORIGEN-predicted ratios; this demonstrates the ability of RAPID to accurately assess isotopic ratios of radioactively decaying isotopes at low levels.

$$N(t) = N_0 \exp(-\lambda * t) \quad (16)$$

$$\lambda = \ln(2)/t_{1/2} \quad (17)$$

Lastly, to visually compare measurements between offline and online ICPMS to ORIGEN, Figure 51 below shows an offline ICPMS mass spectrum scan (gray lines), overlaid with offline measurements (red squares), online measurements (black circles), and the predicted ORIGEN masses (blue dotted line). In order to compare the online and offline measurements to the mass spectrum scan, every set of isobars had to be summed (i.e. mass 147 = ^{147}Nd + ^{147}Pm + ^{147}Sm) from the online measurements. Looking at this data without separation, no differentiation can be made

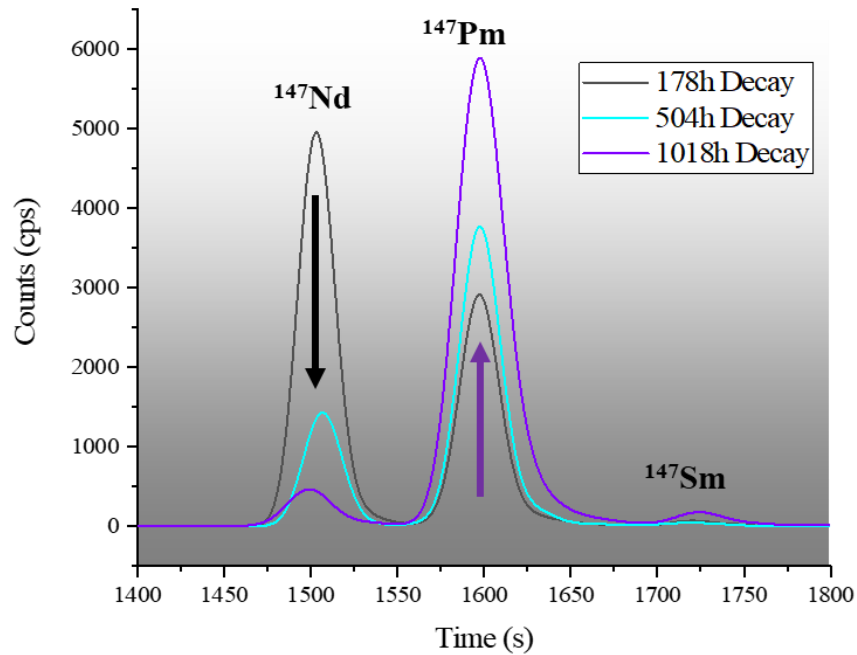


Figure 50. RAPID measurements of m/z 147 as a function of time post-irradiation.

Table 35. Measured vs. ORIGEN-predicted atom percent ratios for neodymium at the three different analysis times post-irradiation, with three ratios shifting either up or down due to radioactive decay²¹².

Time Post Irradiation (h)	178		504		1018	
Isotope Ratio	RAPID (meas. at. %) (2σ, n=3)	ORIGEN (calc. at. %)	RAPID (meas. at. %) (2σ, n=3)	ORIGEN (calc. at. %)	RAPID (meas. at. %) (2σ, n=3)	ORIGEN (calc. at. %)
¹⁴³ Nd/ ¹⁴⁶ Nd ↑	0.46(2)	0.48	1.23(3)	1.25	1.70(4)	1.74
¹⁴⁴ Nd/ ¹⁴⁶ Nd ↑	0.038(4)	0.033	0.12(3)	0.093	0.18(3)	0.18
¹⁴⁵ Nd/ ¹⁴⁶ Nd −	1.36(6)	1.31	1.322(8)	1.31	1.33(3)	1.31
¹⁴⁷ Nd/ ¹⁴⁶ Nd ↓	0.47(2)	0.47	0.19(6)	0.19	0.051(6)	0.051
¹⁴⁸ Nd/ ¹⁴⁶ Nd −	0.56(3)	0.56	0.58(4)	0.56	0.57(1)	0.56
¹⁵⁰ Nd/ ¹⁴⁶ Nd −	0.24(2)	0.22	0.22(3)	0.22	0.22(1)	0.22

↓↑— represent decaying, ingrowing, and static numerator respectively.

between isobars, which is incredibly important in fission product analysis where such a complex set of isotopes exists, in addition to other interfering factors, such as xenon, krypton, or doubly-charged ²³⁵U (all noted in Figure 51). Doubly-charged ²³⁵U creates a signal of m/z 117 and 118, which can cause interferences on isotopes of tin or cadmium.

Offline ICPMS analysis may be able to provide a broader measurement of a sample (more elements) than RAPID, however, without the differentiation between isobars (e.g. ¹⁴³Nd vs. ¹⁴³Pm), no isotopic signatures can be generated. To generate these signatures, i.e. for nuclear forensic analysis, chemical separations are a necessity, and RAPID provides a very quick sample analysis utilizing online ICPMS measurements immediately following separation.

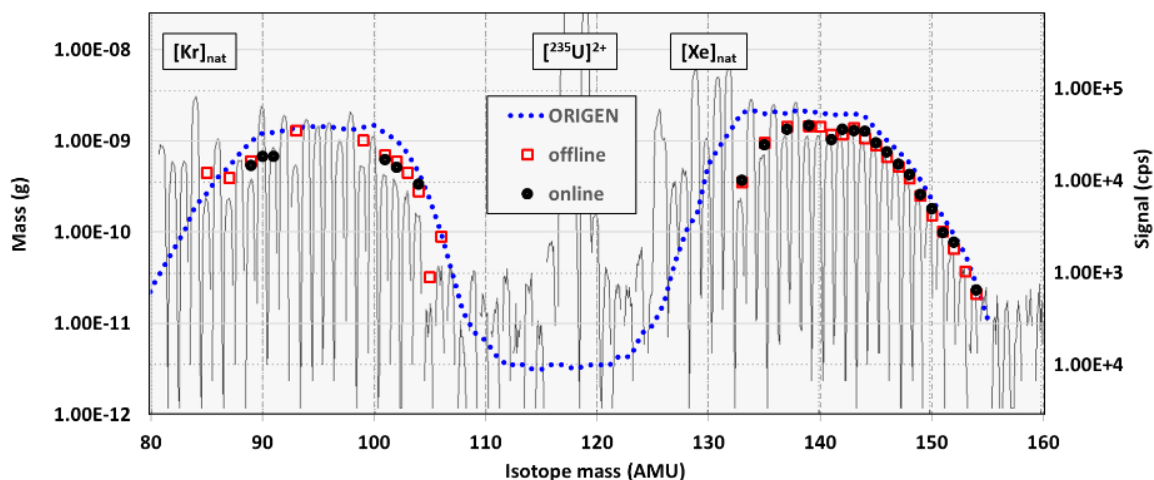


Figure 51. The resulting fission product “double hump curve” as produced by an offline ICPMS mass spectrum scan with offline and online measurements (and ORIGIN predictions) overlaid²¹².

6.5 RAPID’s Nuclear Forensics Analytical Gap

Due to the complexity and multitude of fission products produced in these irradiated HEU samples, there exists more than one type of analysis that can be used. For example, the majority of the fission products produced are stable, or beta emitters, but the minority that are gamma-emitting can be measured with gamma spectrometry (e.g. ⁹⁵Zr, ⁹⁹Mo, ¹³⁷Cs). During the analysis of the third irradiated HEU target, it was discovered that while most of the fission products can be measured with RAPID, some exist in quantities below the detection limits of the method, or those which have not been satisfactorily separated with the current separation scheme. Conversely, gamma spectrometry cannot be used alone to quantify all the fission products produced by irradiation of HEU; the high-activity, short-lived fission products can prevent the measurement of lower-activity isotopes in the first rounds of analysis.

To exemplify this, Figures 52 & 53 below show two gamma spectra from the irradiated HEU in 2018 with the 662 keV ¹³⁷Cs gamma highlighted. The first measurement, performed less than a

week after irradiation, had to use a large dilution of the original sample to maintain an operable dead time of the detector (final dead time of the dilution was still ~7.5%) due to the high activity of the short-lived fission products. Because of this, the ^{137}Cs peak could not be quantified even though it was known to be in the sample. However, the next measurement displayed below (Figure 53), obtained approximately six weeks after the first measurement (with a dead time of ~0.6%), illustrates the existence of the 662 keV gamma.

For this measurement of HEU fission products, both RAPID and HPGe measurements were utilized, one method complementarily filling in the analytical gap left by the other. Table 36 shows this instrumental cooperation and the isotopes measured with each of the methods; notably, the middle column lists gamma-emitting isotopes that were quantified with RAPID rather than HPGe, and the asterisks denote isotopes confirmed with both methods. For the final masses (using RAPID and HPGe) and comparison to ORIGEN, refer back to Tables 30 & 31 in the previous section.

Thus, development of a method which combines RAPID (i.e. ICPMS/chemical separation) and gamma spectrometry would be very useful for an all-inclusive, rapid turnaround fission product analysis. To fill this need, a CZT gamma detector was purchased and an inline system was designed (see section 4.1 for further detail) to obtain gamma spectra of radioactive samples post-separation, pre-ICPMS detection. This capability allows for acquisition of elementally-isolated gamma spectra, without the majority of the other gamma-emitters cluttering up the spectra (post background-subtraction).

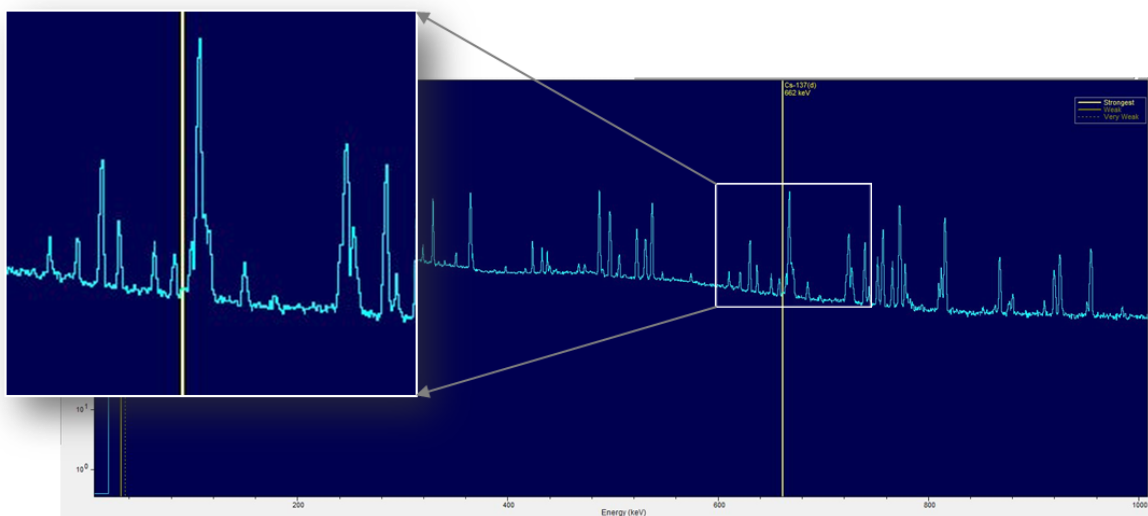


Figure 52. The HPGe measurement of irradiated HEU in October 2018. Inset: the lack of a 662 keV gamma from ^{137}Cs .

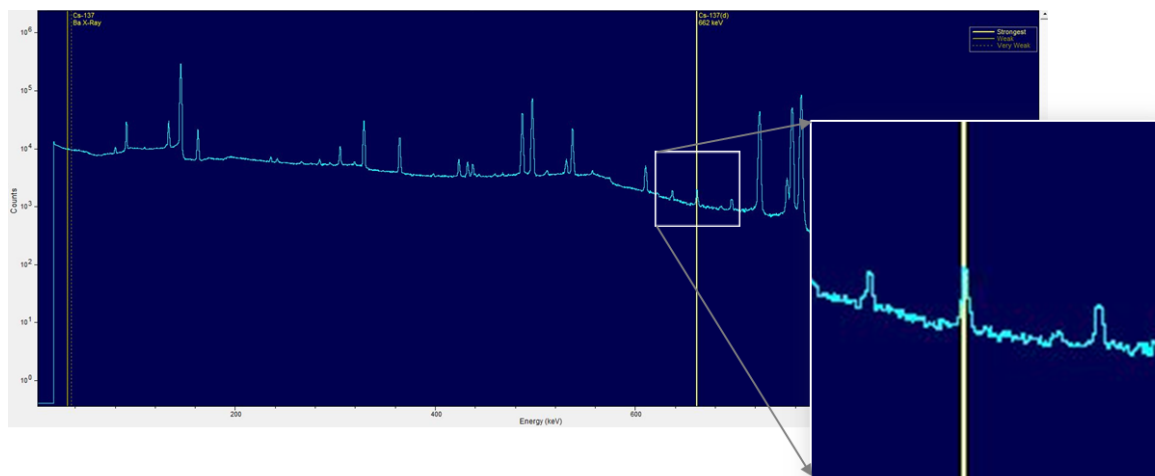


Figure 53. The HPGe measurement of irradiated HEU in November 2018. Inset: the existence of a ^{137}Cs gamma.

Table 36. HEU fission product isotopes quantified with each analytical technique. *isotopes quantified with both techniques.

HPGe	HPIC-ICPMS (radioactive)	HPIC- ICPMS
⁹⁵ Nb	⁸⁹ Sr	¹⁰¹ Ru
⁹⁵ Zr	⁹⁰ Sr	¹⁰² Ru
⁹⁷ Nb	⁸⁹ Y	¹⁰⁴ Ru
⁹⁷ Zr	⁹¹ Y	¹³³ Cs
⁹⁹ Mo	¹³⁵ Cs	¹³⁹ La
^{99m} Tc	¹³⁷ Cs	¹⁴⁰ La*
¹⁰³ Ru	¹⁴³ Pr	¹⁴⁰ Ce
¹⁰⁵ Rh	¹⁴⁷ Pm	¹⁴¹ Ce*
¹²⁷ Sb	¹⁵¹ Sm	¹⁴² Ce
¹³¹ I		¹⁴³ Ce*
¹³² I		¹⁴⁴ Ce*
¹³² Te		¹⁴¹ Pr
¹³³ I		¹⁴³ Nd
¹⁴⁰ Ba		¹⁴⁴ Nd
¹⁴⁰ La*		¹⁴⁵ Nd
¹⁴¹ Ce*		¹⁴⁶ Nd
¹⁴³ Ce*		¹⁴⁷ Nd*
¹⁴⁴ Ce*		¹⁴⁸ Nd
¹⁴⁷ Nd*		¹⁵⁰ Nd
¹⁴⁹ Pm*		¹⁴⁹ Pm*
		¹⁴⁹ Sm
		¹⁵² Sm
		¹⁵³ Sm
		¹⁵⁴ Sm

CHAPTER 7: DEVELOPMENT OF AN INLINE CZT DETECTION SYSTEM

This chapter will describe the method development performed for the novel inline CZT work for this PhD, specifically the initial setup and testing, MCNP modeling, and two different fission product sample analyses. These samples demonstrate two capabilities of this system, depending on the level of gamma activity of the sample.

The first section will summarize the article published in JRNC describing the proof-of-concept inline gamma detection of fission product elements post chemical separation²¹⁴.

7.1 JRNC Publication

Due to the complication of highly radioactive fission products causing large amounts of dead time in gamma detection systems, which can prevent analysis of the complete suite of fission products generated shortly after irradiation, an inline gamma detection system to RAPID was proposed and designed. This inline system inserts a CZT detector directly after the HPIC, but before the ICPMS within the RAPID configuration. This capability allows for acquisition of elementally-isolated gamma spectroscopy, and the paper presents a test of its quality and utility, specifically relating to fission products.

Obtaining gamma spectra after elemental separation should lower the detection limit of each isotope (determined by the activity of the isotope), due to the lack of interfering gammas. If the activity of the isotope is low, the HPIC pumps can be manually stopped, allowing for additional dwell time around the detector. If the activity is sufficiently high, a transient “gamma

chromatogram” can be acquired, which is a gamma spectrum as a function of time, analogous to a mass chromatogram obtained with an ICPMS.

In this work, elementally-isolated gamma spectra are presented from a low activity (decayed used nuclear fuel) and a higher activity sample (aqueous waste from an ORNL ^{238}Pu process) with various fission products, with additional spectra using a fraction collector and an HPGe for high-resolution spectra. Each sample was screened with HPGe and RAPID before inline CZT analysis for confirmation of each element and expected gamma signatures, in addition to establishing agreement between three different analytical methods.

The main gamma-emitting elements from the low-activity sample were cesium, cerium, and europium, and a correlating spectrum for each was acquired post-separation with a 5-min dwell time. A fraction collector was used to collect individual fractions for HPGe gamma analysis for comparison to the CZT inline spectra. Additionally, observation of the ingrowth of $^{137\text{m}}\text{Ba}$ after the Cs/Ba separation was made and illustrated, which, due to the short (2.5 min) half-life of $^{137\text{m}}\text{Ba}$, cannot be performed without an inline separation/detection capability. For the higher activity sample, the main gamma-emitting elements were cesium, cerium, europium, and ruthenium, and a gamma chromatogram was acquired along with individual spectra for cerium, europium, and ruthenium (30 s dwell time).

This test successfully demonstrated the additional analytical capability that inline gamma spectroscopy adds to the RAPID method by combining chemical separation, gamma detection, and mass spectrometry to fully characterize irradiated nuclear materials in a short period of time. It is ideal for short-lived fission product analysis, especially those that exist below the detection limit of an ICPMS.

7.2 Method Development

In order to begin this experiment, the CZT had to be tested and other equipment selected to operate the CZT: the most compact equipment which could be used in this situation is a unit which can provide both high voltage and a multi-channel analyzer. The Canberra Lynx was selected for these experiments, and it and a laptop were moved to the necessary lab after successful testing of the CZT. The Lynx has several types of acquisition modes, and two were used for these experiments: pulse height analysis (PHA) and multi-spectral scaling (MSS). PHA was used for singular long-dwell acquisitions, while MSS allowed for continuous acquisition of spectra at a user-specified rate, saving into a buffer within the software. The next step was calibration of the detector within the lab/fume hood; unfortunately, no liquid radiation sources strong enough for a good calibration in the sample loop configuration were in NACIL inventory. Thus, for the calibration, button sources of ^{133}Ba and ^{137}Cs were used, giving a calibration good to 662 keV.

The first experiment utilized a sample of used nuclear fuel, with a burnup of ~10%, which provided both medium- and short-lived gamma-emitting fission products. To begin, both RAPID and HPGe analysis were performed on the sample to qualitatively assess what the CZT should be able to measure and that RAPID can separate. Table 37 lists the isotopes observed in the HPGe measurement – highlighted are the isotopes that fall within the CZT calibration (<662 keV) and are separated by RAPID. Figure 54 illustrates the subsequent RAPID separation (note the peak broadening due to the additional 30 s loop around the CZT). From this data, three elements were selected: cesium, cerium, and europium.

The next step for this experiment was to measure the sample with the CZT: first as an unseparated sample in its sample vial and second, as an unseparated sample in the loop configuration. The two configurations should give identical data except for the 20x dilution that occurs with the injection

Table 37. Gamma-emitting isotopes in the fuel sample (bolded isotopes are within CZT calibration and readily separated)

Isotope	γ (keV)	Isotope	γ (keV)
⁹⁵ Zr	724.2	¹³⁷ Cs	661.7
	756.7	¹⁴⁴ Ce	80.1
¹²⁵ Sb	427.9		133.5
	600.5	¹⁴⁵ Sm	60.9
¹³⁴ Cs	475.4	¹⁵⁴ Eu	123.1
	563.2		723.4
	569.3		873.2
	604.7	¹⁵⁵ Eu	86.5
	795.9		105.3
	801.9	²⁴¹ Am	59.5

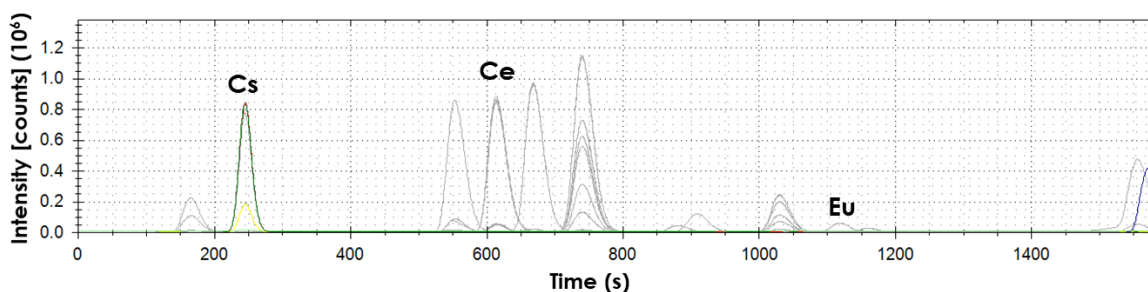


Figure 54. RAPID data for the fuel sample with the selected elements labeled.

into the sample loop. After confirmation that the expected gammas can be seen with the CZT (at a higher concentration than generally used for regular ICPMS analysis), several separations were performed with gamma spectra acquisition. It was discovered that, due to the sample's relatively low activity, the separated elements needed to have additional dwell time around the CZT to generate enough counts for an identifiable spectrum. For this initial test (and sample), a dwell time of five minutes was chosen (using PHA); of note, for every length of dwell time selected to acquire data, a corresponding-length background spectrum was obtained. For the next test, a sample (from

REDC) with more gamma activity and a shorter decay time than the used nuclear fuel was analyzed. This sample was an aliquot of aqueous waste (AW) from a ^{238}Pu production process, and it had a higher gamma activity level than the previous sample analyzed with the CZT. The transuranium analytical laboratory (TAL) group within NACIL (located at the REDC) provided this aliquot of AW, and results from their HPGe analysis are given in Table 38. The isotopes that emit gammas within the CZT's sensitivity/calibration range ($<700\text{ keV}$) and separated by RAPID are highlighted in red. Sample preparation involved a series of dilutions, which lowered the activity seen by the CZT; however, the approximate injected ($50\text{ }\mu\text{L}$ are injected for each separation) activities are provided in Table 39 for each of the highlighted isotopes, also accounting for the radioactive decay between the initial HPGe analysis and the subsequent CZT analysis. It can be seen that between the elements injected, there are several orders of magnitude of gamma activity (from 15 nCi of ^{243}Am to $26\text{ }\mu\text{Ci}$ of ^{144}Ce). The ratios within each element are as follows: $^{106}\text{Ru}/^{103}\text{Ru}$ (16.9), $^{137}\text{Cs}/^{134}\text{Cs}$ (6.8), $^{144}\text{Ce}/^{141}\text{Ce}$ (133.9), and $^{155}\text{Eu}/^{154}\text{Eu}$ (1.7). Each of these gives an approximate ratio to compare to once the chemically-isolated gamma spectra are acquired.

Due to the higher gamma activity (compared to the fuel sample), no additional dwell time at the detector was necessary, and gamma spectra were acquired every 30 s (using MSS) to compile a transient gamma energy spectrum as a function of time during the separation. Several spectra were acquired with this AW sample, including a five-minute unseparated CZT spectrum and four transient runs with the 30 s spectra.

As the data output from the Lynx is a text file, several types of software can be used to display the acquired spectra. In the following sections, ORIGIN Lab, GADRAS (gamma detector response and analysis software), and PeakEasy were utilized to view the various spectra. ORIGIN also has data analysis capabilities, but for this work, only a smoothing function was used to make the CZT

spectra easier to view. The smoothing function employed was the Savitzky-Golay method²¹⁵, which seeks to preserve peak shape, and it was decided to use a window of 20 data points with a polynomial function of the 2nd order.

Table 38. HPGe measurements of the AW from the TAL, performed on 7/25/2019. Highlighted in red are isotopes that should be identifiable by CZT and separated with RAPID.

Isotope	Bq/mL	Error (Bq/mL)
⁶⁰ Co	7.8E+05	0.9E+5
⁹⁵ Nb	1.8E+08	0.1E+8
⁹⁵ Zr	3.7E+08	0.1E+8
¹⁰³ Ru	1.1E+08	0.1E+8
¹⁰⁶ Ru	5.7E+08	0.2E+8
^{110m} Ag	4.1E+05	0.7E+5
¹²⁵ Sb	5.0E+06	0.4E+6
¹³¹ I	< 4.3E+05	
¹³⁴ Cs	5.2E+06	0.2E+6
¹³⁷ Cs	3.3E+07	0.1E+7
¹⁴⁰ Ba	< 2.1E+06	
¹⁴⁰ La	< 1.7E+05	
¹⁴¹ Ce	3.7E+07	0.1E+7
¹⁴⁴ Ce	1.2E+09	0.1E+9
¹⁵⁴ Eu	1.7E+06	0.2E+6
¹⁵⁵ Eu	2.9E+06	0.2E+6
¹⁵⁶ Eu	< 1.7E+06	
²³³ Pa	1.1E+06	0.5E+6
²³⁷ Np	< 1.0E+07	
²³⁹ Np	< 6.8E+05	
²⁴¹ Am	< 3.6E+05	
²⁴³ Am	5.6E+05	1.5E+5

Table 39. Approximate injected activities for each isotope per CZT analysis (performed on 10/8/2019) in both curies and becquerels.

Isotope	μCi injected	Bq injected
^{103}Ru	0.760	2.81E+04
^{106}Ru	12.880	4.77E+05
^{134}Cs	0.126	4.67E+03
^{137}Cs	0.854	3.16E+04
^{141}Ce	0.194	7.19E+03
^{144}Ce	25.984	9.61E+05
^{154}Eu	0.043	1.61E+03
^{155}Eu	0.073	2.71E+03
^{243}Am	0.015	5.38E+02

7.3 Results and Discussion

7.3.1 MCNP Simulated Spectra

The goal of modeling the CZT detector in MCNP was to observe the spectral shape of elementally pure gamma spectra and overall qualitative comparison to the experimental CZT data. To do this qualitative comparison, four source definitions were created to match the experimental spectra: $^{133}\text{Ba} + ^{137}\text{Cs}$, $^{103}\text{Ru} + ^{134}\text{Cs}$, $^{141}\text{Ce} + ^{144}\text{Ce}$, and $^{154}\text{Eu} + ^{155}\text{Eu}$. An example input deck is included in the appendix for reference. Source definitions were defined based on each isotope's gamma emissions and their relative intensities, shown in Table 40. The $^{133}\text{Ba}/^{137}\text{Cs}$ source definition card was created as a point source since it was created to compare to the button sources used for energy calibration of the CZT. However, the other three sources were modeled as the loop source, described in section 4.2.2. Additionally, the latter three sources were modeled after the AW sample; to create a more accurate comparison, the combination of isotopes as expected in each separated spectrum was modeled (e.g. ruthenium and cesium elute at almost the same time, so thus $^{103}\text{Ru} + ^{134}\text{Cs}$).

Table 40. Source definitions used in MCNP input files, shown as gamma energies and relative intensities.

Cs-134		Ce-144		Eu-154		Ba-133			
<i>keV</i>	<i>Int.</i>	<i>keV</i>	<i>Int.</i>	<i>keV</i>	<i>Int.</i>	<i>keV</i>	<i>Int.</i>		
604.721	9.76E-01	133.515	1.11E-01	123.0706	4.04E-01	356.0129	0.6205		
795.864	8.55E-01	80.12	1.36E-02	1274.429	3.48E-01	80.9979	0.329		
569.331	1.54E-01	40.98	2.57E-03	723.3014	2.01E-01	302.8508	0.1834		
801.953	8.69E-02	33.568	2.00E-03	1004.76	1.80E-01	383.8485	0.0894		
563.246	8.34E-02	36.027	4.50E-02	873.1834	1.21E-01	276.3989	0.0716		
1365.185	3.02E-02	35.551	2.46E-02	996.29	1.05E-01	30.973	0.602		
1167.968	1.79E-02	Ce-141 <i>keV</i> <i>Int.</i> 145.44334.84E-01 36.0278.89E-02 35.5514.87E-02		247.929	6.89E-02	30.625	0.326		
475.365	1.48E-02			43.996	1.32E-01	Cs-137 <i>keV</i> <i>Int.</i> 661.6570.851 283.55.8E-04 32.1930.0367 31.8160.0199			
1038.61	9.90E-03			42.308	7.32E-02				
29.778	1.20E-06			591.8	4.95E-02				
29.458	6.00E-07			1128.6	3.17E-03				
Ru-103 <i>keV</i> <i>Int.</i> 497.0859.10E-01 610.3335.76E-02 557.0578.41E-03 53.2864.43E-03 443.813.39E-03 20.2154.90E-02 20.0732.60E-02				Eu-155 <i>keV</i> <i>Int.</i> 86.54793.07E-01 105.30832.11E-01 45.2991.31E-02 60.00861.22E-02 42.9961.20E-01 42.3086.69E-02					

Once the MCNP calculations were performed, the resulting F8 tally (i.e. gamma spectra as a normalized probability) for each isotope was multiplied by the corresponding injected activity (see Table 39) converted to becquerels. By doing this and plotting the two isotopes which elute at the same time on the same graph, the relative gamma peaks can be observed as they should be seen with the CZT detector.

The effects of the peak broadening (discussed in section 4.2.2) are illustrated in Figure 55 with the Ba/Cs source spectrum. The fit for the peak broadening function used in this MCNP model does not perfectly match the acquired calibration spectrum (which will be shown in the next section), but since the fit was calculated from actual CZT data, and no other CZT F8 broadening functions

can be found in the literature, it will be used for the remainder of the spectra. The main purpose of it is to accurately simulate the broadening that occurs in the detector during acquisition, making it more realistic for a spectral shape comparison between modeled and experimental spectra.

Since the calibration is only good until 662 keV (and the CZT efficiency rapidly decreases around that energy), the main peaks that will be visible in the experimental data, and thus viable to compare to, will be <700 keV. However, Figures 56–59 show all peaks that are signature to the selected isotopes for a full illustration of what to expect with a chemically separated gamma spectrum.

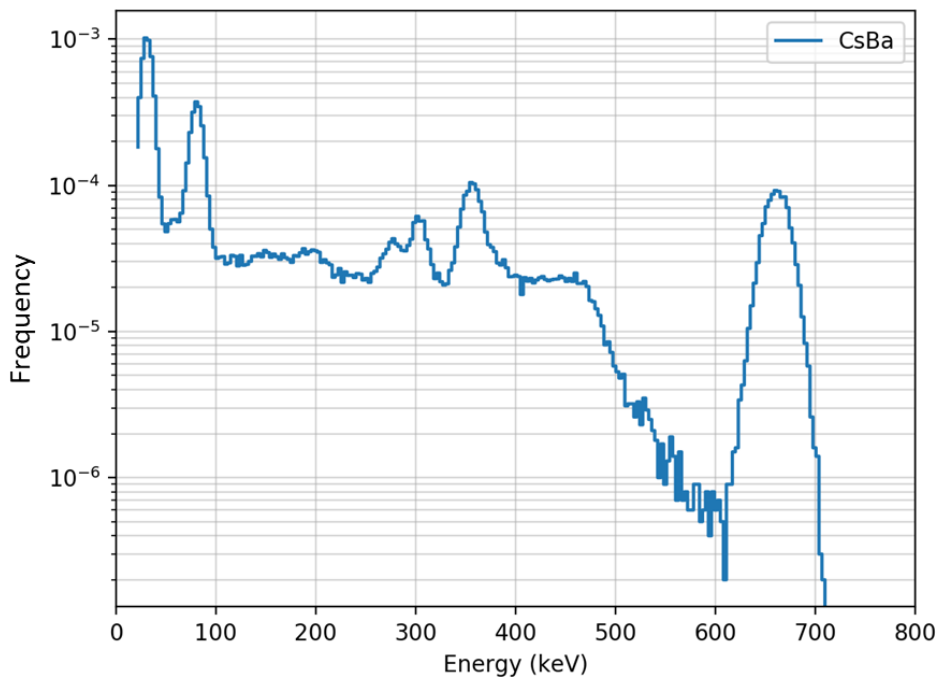


Figure 55. MCNP-generated $^{133}\text{Ba} + ^{137}\text{Cs}$ point source spectrum.

For the first fraction, where ruthenium and cesium elute, Figure 56 illustrates the predicted spectrum – notably, ^{137}Cs and ^{106}Ru do not have any direct gamma emissions, rather, their gammas result from the beta decays from $^{137\text{m}}\text{Ba}$ and ^{106}Rh respectively. Due to this fact, only ^{103}Ru and ^{134}Cs were modeled for this spectrum. It can be seen that the main peaks expected are the 497 keV from ^{103}Ru , a combined peak at around 600 (605 from ^{134}Cs and 610 from ^{103}Ru), and possibly the 800 keV from ^{134}Cs , depending on the CZT's efficiency at that energy. Due to the lack of resolution at 600 keV, there will be multiple peaks there that will not be distinguishable from each using the CZT. Lastly, the x-rays from ^{103}Ru (20 keV) may be visible in the experimental spectra, as the resolution and efficiency are both good in that energy region using a CZT, however, that is not seen with this modeled data due to the imperfect peak broadening function. To generate more accurate predictions for the x-ray energy range, the peak broadening F8 tally function would have

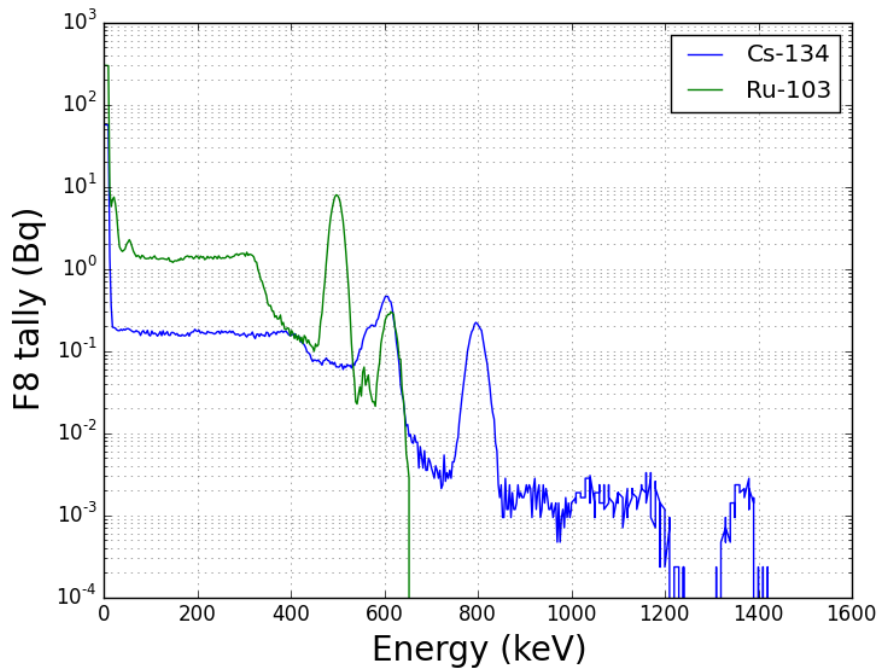


Figure 56. MCNP-generated $^{103}\text{Ru} + ^{134}\text{Cs}$ spectrum, showing both spectra overlaid at their relative intensities to each based off of Bq in the injected sample.

to be calculated with higher fidelity. That task of generating more accurate x-ray models for the CZT was not performed for this work, as these models were generated to visually compare the spectral shape of select elutions off of the column for this sample.

The next elution off of the column is the cerium fraction, so a spectrum was generated showing gamma emissions from both ^{141}Ce and ^{144}Ce in relative proportions from this sample. Figure 57 shows that these two spectra are nearly identical, besides the peak at 80 keV from ^{144}Ce and the intensity difference due to $^{144}\text{Ce}/^{141}\text{Ce}$ being over 100 (thus a two-magnitude difference between the two spectra). Once again, the modeled x-ray region does not have the resolution to accurately predict the CZT response for this sample.

Lastly, the final elution modeled for this sample was the europium fraction, containing a near one-to-one mix of ^{154}Eu and ^{155}Eu . Figure 58 illustrates the full spectrum of ^{154}Eu , which is comparable

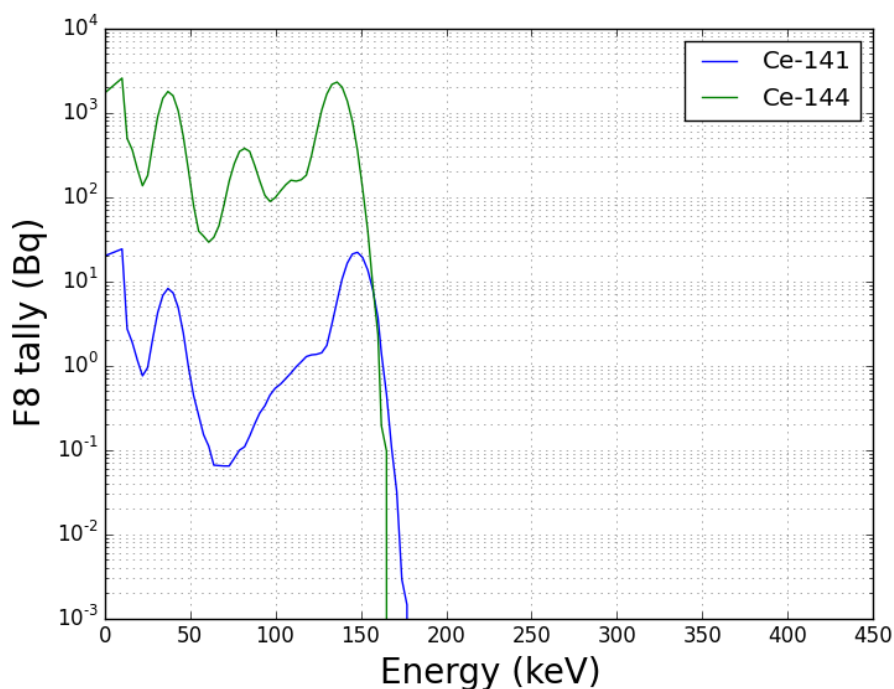


Figure 57. MCNP-generated $^{141}\text{Ce} + ^{144}\text{Ce}$ spectrum, showing both spectra overlaid at their relative intensities to each based off of Bq in the injected sample.

to what an HPGe can measure (with better resolution), however, Figure 59 shows the more likely spectra to be seen with the CZT, given its inability to detect high-energy gammas ($> \sim 700$ keV). Six peaks are visible, with five below 150 keV, including the ~ 43 keV x-ray emitted by both isotopes. Depending on the low-energy resolution of the CZT, the three separate peaks at 86, 105, and 123 keV may or may not be discernable in the actual spectrum. If using an HPGe, it can be expected that all the high-energy gammas will be observed as seen in Figure # (i.e. 873, 996, 1003 keV, and more from ^{154}Eu), though the x-ray resolution may differ from that of the CZT. These differences will be illustrated in later sections within this chapter.

To better compare with the experimental spectra, each of these spectra was summed accordingly (i.e. $^{134}\text{Cs} + ^{103}\text{Ru}$, $^{141}\text{Ce} + ^{144}\text{Ce}$, and $^{154}\text{Eu} + ^{155}\text{Eu}$), and will be presented in the appropriate section.

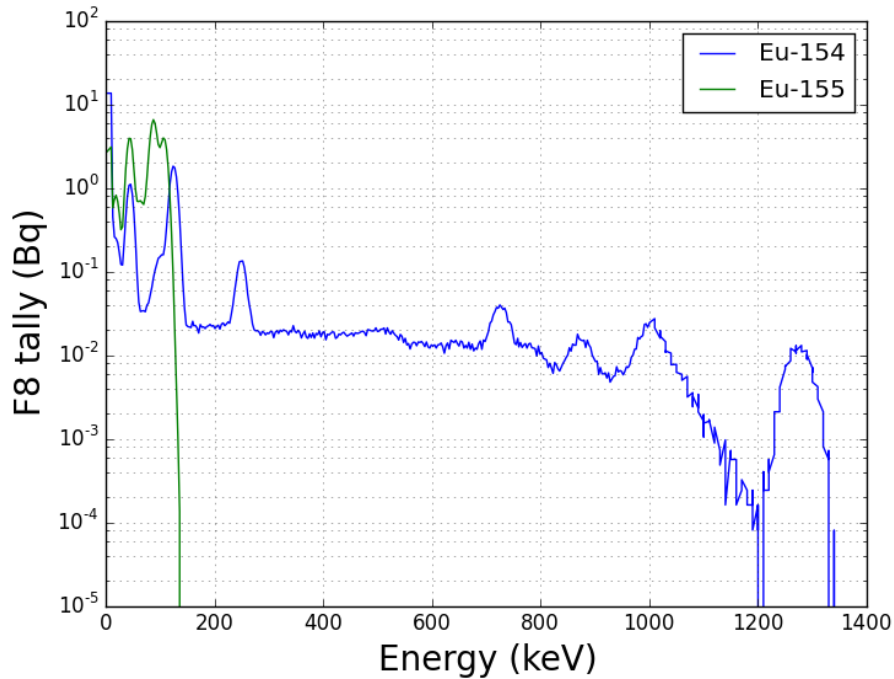


Figure 58. MCNP-generated $^{154}\text{Eu} + ^{155}\text{Eu}$ spectrum, showing both spectra overlaid at their relative intensities to each based off of Bq in the injected sample.

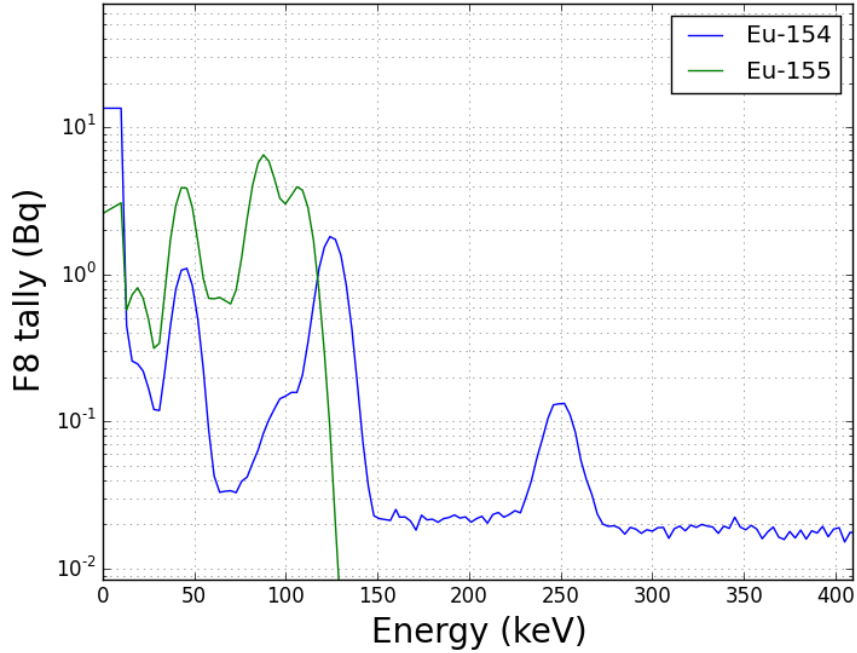


Figure 59. A magnified view of the MCNP-generated europium spectra in Figure 58.

7.3.2 Long Dwell Time CZT Measurements Post-Separation

To calibrate the CZT detector, two button sources of $^{133}\text{Ba} + ^{137}\text{Cs}$ were placed directly in front of the detector and counted for one hour. The resulting spectrum is shown in Figure 60, displayed using GADRAS, and the low-energy tail can be seen on those peaks, as expected from a CZT detector. This spectrum was used for the calculation of the peak broadening fit function for MCNP as described in section 4.2.2. Comparing back to Figure 55, the MCNP-generated Cs/Ba spectrum, it can be seen that the experimental CZT obtained better resolution and thus more peaks were distinctly visible with the CZT than predicted. Once again, the main way to correct this discrepancy would be to iterate further on the peak broadening function provided in MCNP compared to the actual CZT data, which was not a focus for this project.

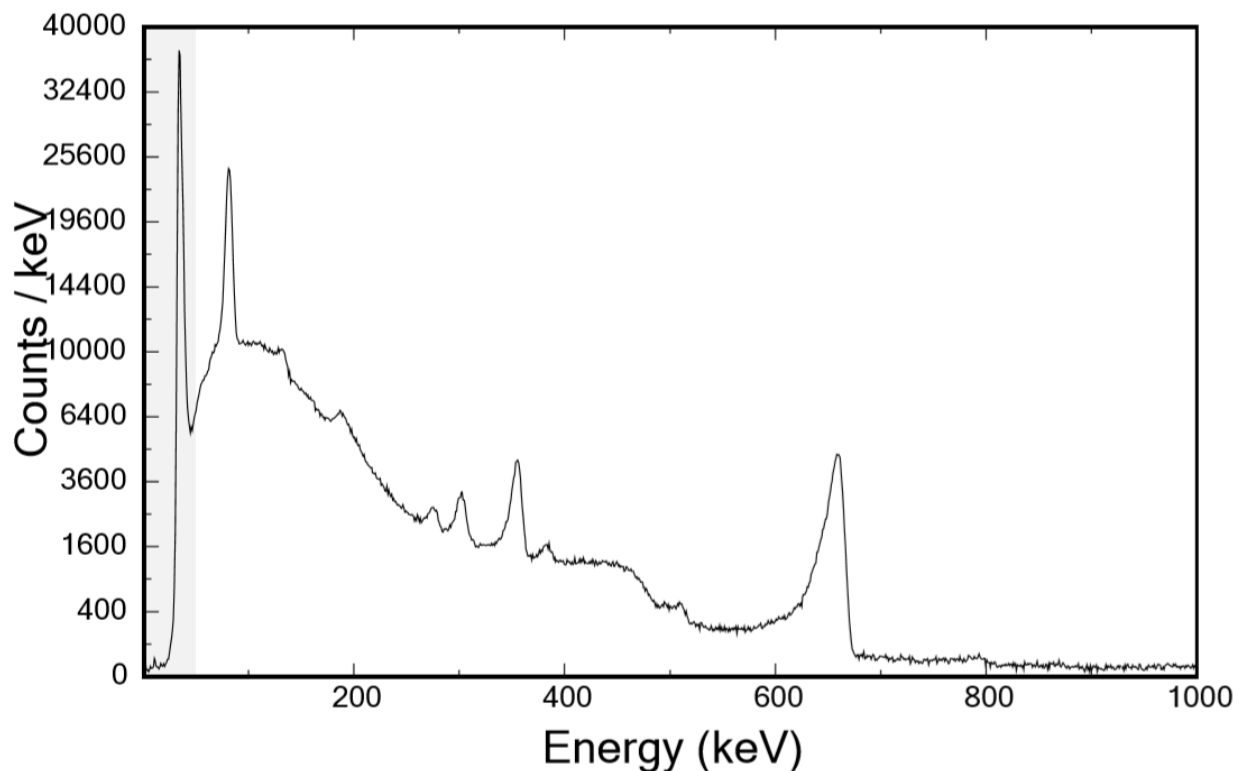


Figure 60. Spectrum of $^{133}\text{Ba} + ^{137}\text{Cs}$ button sources for calibration purposes.

The same sources were used periodically (i.e. once every week or two) to verify the quality of the calibration and to make sure it did not drift at all. This CZT did not drift from the initial calibration through the several months of measurements, however, a more ideal calibration process would have utilized a multi-element source in liquid form as to conform to the same sample geometry as the source loop around the detector. Nonetheless, these button sources were adequate for calibrating the CZT for these experiments.

The first sample measurement performed with the CZT was an acquisition of the unseparated fuel sample to assess the resolution and efficiency of the CZT and verify which gammas could be identified (compared to the HPGe spectrum). Two different sample configurations were used: the sample vial directly in front of the detector, and an injection of the sample (bypassing the column

but going through a 20x dilution) to fill the sample loop wrapped around the detector. The sample loop was designed to increase interaction time of the sample with the detector to improve overall detectability, so it was assumed that there would be a notable improvement in the solid angle (sample vs. detector) compared to the first configuration. To assess whether this assumption was correct, the spectrum collected with the first configuration was divided by 20 to account for the dilution from injection and compared to the measured loop spectrum (shown in Figure 61). It can be seen that there is an increase from the calculated “vial/20” spectrum to the loop spectrum, and when the two spectra were compared in terms of total counts, it was discovered that this increase was by a factor of ~ 2.4 . This did confirm the advantage that using a sample loop (versus a source directly in front of the detector) provides an additional dwell time and increase in solid angle in the system.

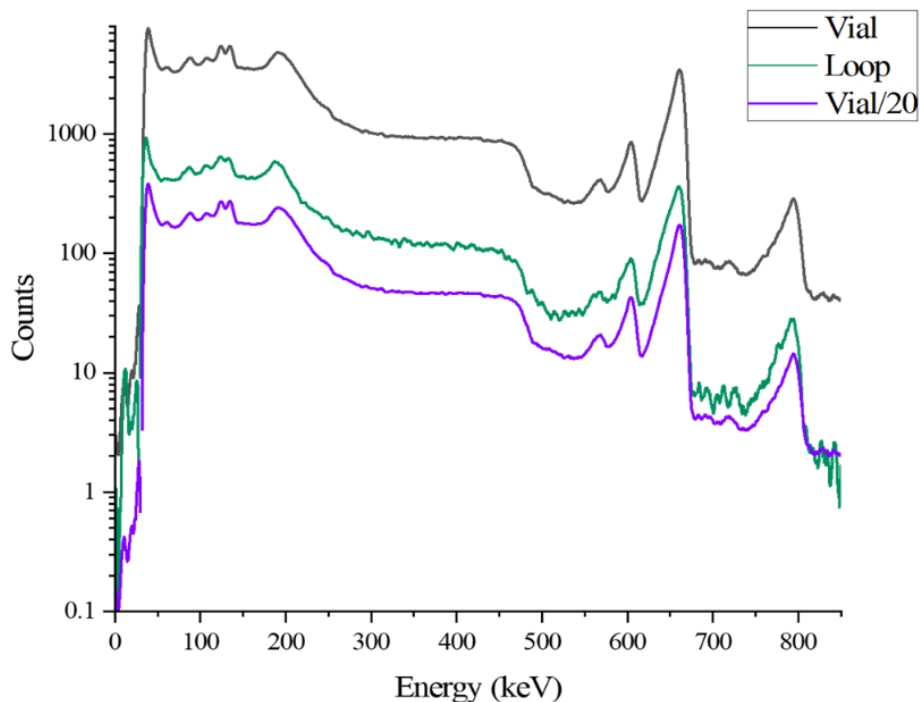


Figure 61. Smoothed CZT gamma spectra of the unseparated fuel sample in two configurations: vial and loop. The loop configuration is a 20x of the vial concentration (calculated spectrum shown in purple for comparison).

Referring back to section 7.2, it is known that the fuel sample has a very similar composition to that of the AW sample modeled in the previous section (minus ruthenium and ^{141}Ce), and the consistencies can be observed. Multiple x-rays can be seen in the <50 keV range (32 keV for cesium, ~35 keV for cerium, and ~43 keV for europium), while the europium peaks are visible from ~80–250 keV, and lastly, the cesium peaks are seen between 500 and 800 keV. Since these spectra were acquired pre-separation, the ^{137}Cs peak (662 keV) is observed at full intensity compared to the ^{134}Cs peaks (569, 604, and 795 keV). Note the unique peak tailing characteristic of the CZT, which is mainly visible in the larger peaks (i.e. the 662 and 795 keV peaks). From this experiment, validation of the CZT operation was confirmed (resolution and peak confirmation compared to the HPGe measurements), the solid angle of the sample loop was demonstrated to obtain higher counts than a source in front of the detector, and it was predicted that spectra post-separation could be easily acquired with cesium, cerium, and europium.

The next test was to inject a fuel sample, perform the separation, and see if the sample's activity was high enough above background to generate a transient gamma chromatogram by using the Lynx's MSS mode on 30 s (acquires one spectrum every 30 s). The resulting gamma chromatogram is shown in Figure 62, where there is no change from background/noise during the entire separation. This chromatogram is generated with GADRAS (in its time history tab), where time-based spectra can be uploaded, and GADRAS presents it as normalized counts per second per detector (data can be uploaded from multiple detectors).

Since no detectable changes in activity were seen with this method, it was decided to stop the HPIC pumps at the appropriate times to acquire five-minute long dwell time spectra of cesium, cerium, and europium (per the data from Table 37 and Figure 54) mid-separation. The elution times of each of these elements is known from the RAPID method development (and confirmed

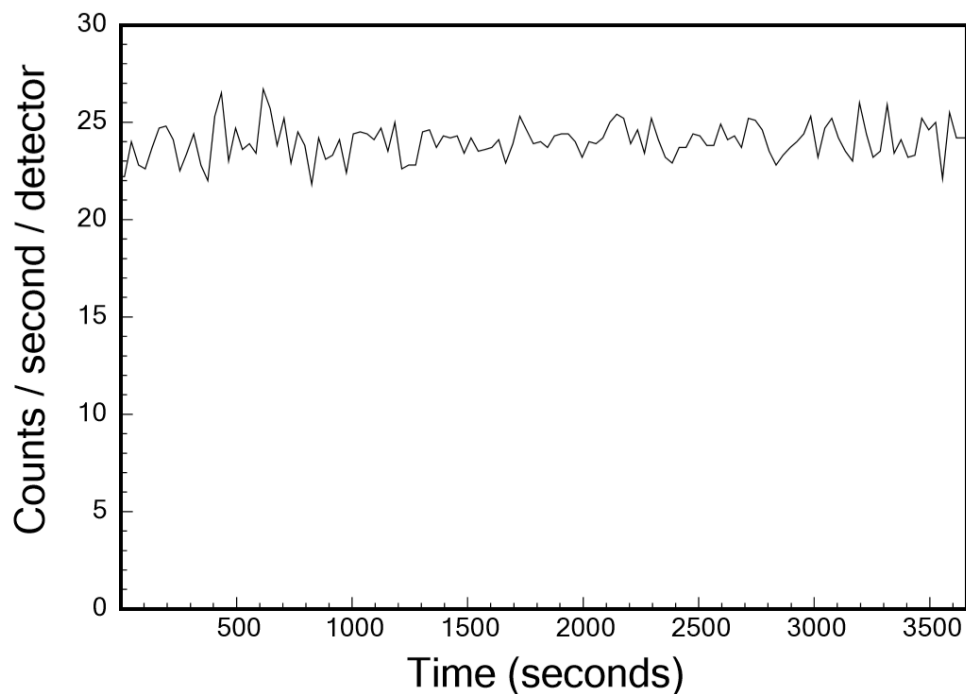


Figure 62. Transient gamma chromatogram of the used fuel sample. Due to the low sample activity, nothing above background can be seen with the sample loop's intrinsic 30 s dwell time.

again for this sample, see Figure 54), and using the ICPMS as a secondary detector, the pumps were stopped for each element as they filled the sample loop. Figure 63 presents these five-minute acquisitions (post background subtraction), where visible peaks can be seen, identifying each element. Each peak can be attributed to an isotope listed in Table 40, where the gamma emissions from each of the isotopes analyzed in this section are given. Additionally, for the cesium spectrum, the Compton edge (~ 480 keV) and plateau (~ 200 keV–480 keV) can be seen for the 662 keV peak, plus the resulting backscatter peak at ~ 200 keV. Compton interactions occur when the incident gamma interacts with an electron in the detector material and loses some of its original energy, depending on the scatter angle, with the maximum energy being the Compton edge. The backscatter peak is created by a gamma interacting with the material around the detector, then scattering back into the detector after that interaction. The equation to calculate the resulting

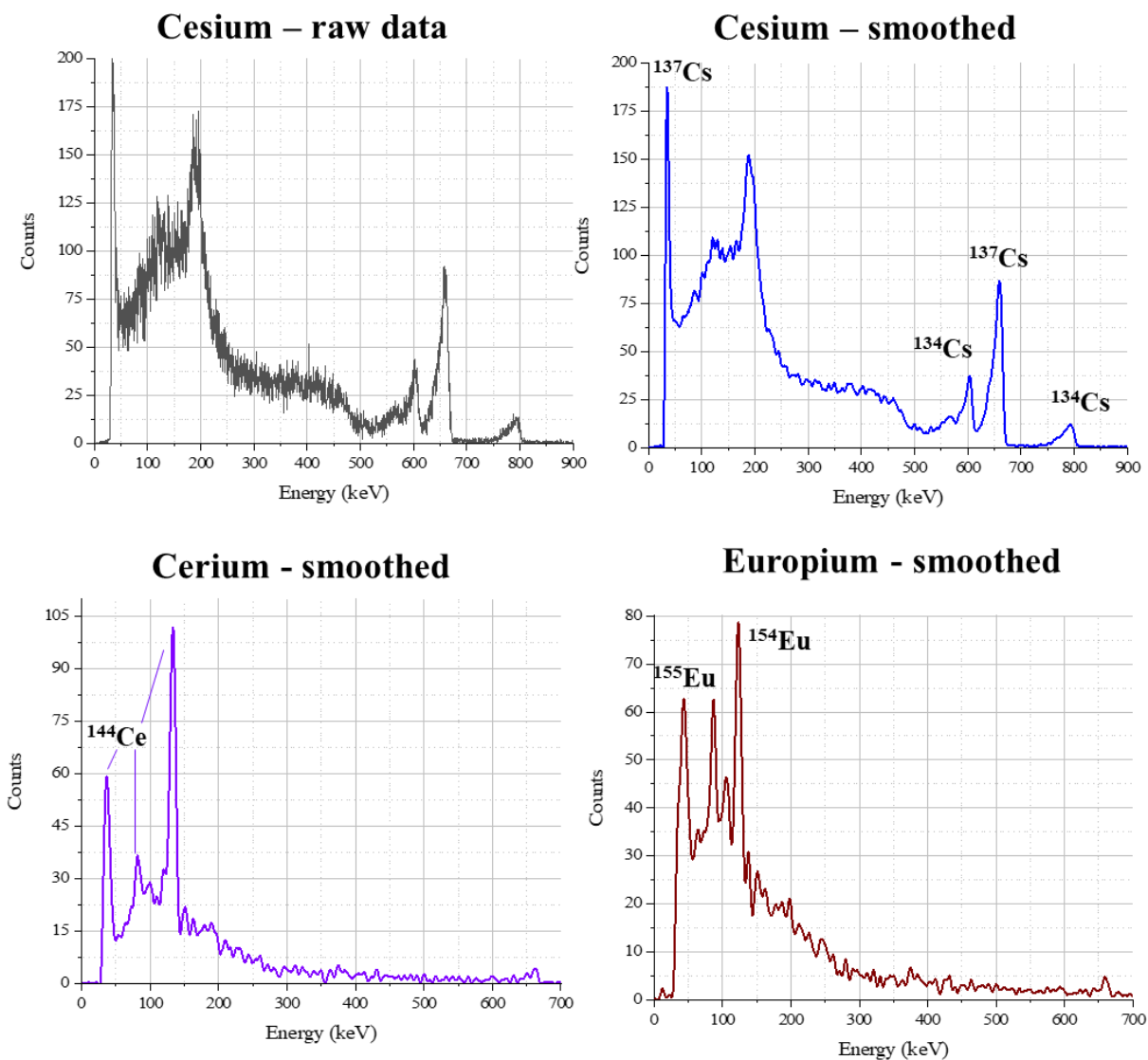


Figure 63. Chemically-separated CZT spectra of cesium (raw data and smoothed data), cerium, and europium in the fuel sample with a dwell time of five minutes.

Compton-scattered gamma energy is given below in Equation 18, where E_0 is the energy of the main gamma (662 keV) and mc^2 is the mass of an electron (511 keV). Using this, and an angle of 180° , a backscatter peak of 185 keV is calculated, which correlates to a Compton edge of 477 keV ($662 \text{ keV} - 185 \text{ keV} = 477 \text{ keV}$), which can be seen in both cesium spectra (Figures 63 and 65).

$$E' = E_0 * [1 + \frac{E_0}{mc^2} * (1 - \cos(\theta))]^{-1} \quad (18)$$

Overall, these resulting spectra (cesium, cerium, and europium) can be compared to the original non-separated spectrum, where it can be seen that all the expected peaks are in both sets of measurements, but the peaks are more discernable in the separated spectra. The overall counts are low (ranging from ~ 15 [^{134}Cs 795 keV] to 180 counts [^{137}Cs 32.2 keV x-ray] in peak height) even with the dwell time of five minutes, however, after background subtraction, the peaks are clearly identifiable. This demonstrates the utility of chemically separating out each element of interest from the rest of the sample, which eliminates conflicting gammas and reduces the overall noise of each spectrum. Additionally, a comparison of raw data to smooth data is given, illustrating the benefits of viewing the spectra after applying the smoothing function. These spectra are the first of their kind: gamma spectra of chemically separated elements with an inline system.

Notably, while performing these 5-min dwell time measurements post-separation, a lower intensity than expected of the ^{137}Cs 662 keV peak was noticed, and it was attributed to the separation between barium and cesium. Since the 662 keV peak is generated by the decay of $^{137\text{m}}\text{Ba}$ to the stable ^{137}Ba (Figure 64), instead of directly by the decay of ^{137}Cs , the chemical separation of cesium and barium separates the 662 keV from the cesium fraction. However, due to $^{137\text{m}}\text{Ba}$'s 2.5 min half-life, once the pumps are stopped, it can start growing back in at that rate. To observe this phenomenon, another experiment was conducted, using the Lynx's MSS mode with a 60 s acquisition rate over eight minutes while the cesium fraction is paused in front of the detector.

Based off of the 2.6-min half-life, the theoretical ingrowth of $^{137\text{m}}\text{Ba}$ over these eight minutes was calculated as a fraction of the ^{137}Cs activity (activity of barium divided by the activity of cesium) using Equation 19. The first term of this transient equilibrium Bateman equation is one because the relatively long half-life of ^{137}Cs (30.1 years) is essentially stable when calculating the change of activity as a function of minutes, and thus the entire term becomes $\exp(0) = 1$. The branching ratio (BR) for this calculation was 94.6% (see Figure 64). By these calculations, it can be seen that there is a factor of ~ 3 (3.22) increase between the first minute and the last minute of ingrowth, which correlates to the increase measured experimentally (Figure 65).

$$\frac{A_{\text{Ba}}}{A_{\text{Cs}}(0)} = \frac{\lambda_{\text{Ba}}}{\lambda_{\text{Ba}} - \lambda_{\text{Cs}}} [1 - (\exp(-t * \lambda_{\text{Ba}}))] * \text{BR} \quad (19)$$

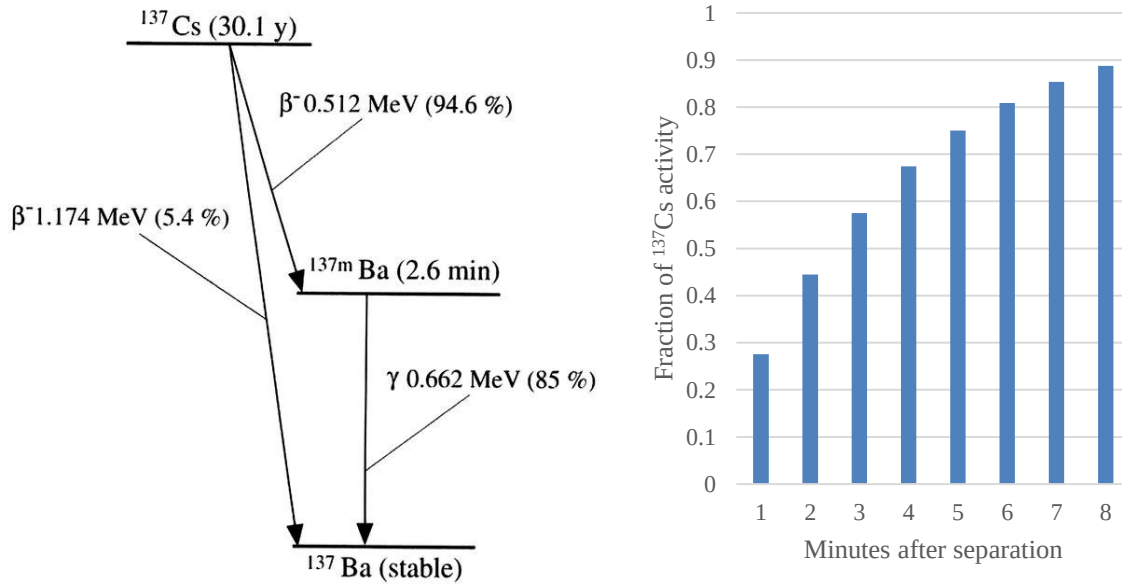


Figure 64. Left: decay scheme of ^{137}Cs . Right: theoretical ingrowth of $^{137\text{m}}\text{Ba}$ given as a fraction of the ^{137}Cs activity as a function of time after separation.

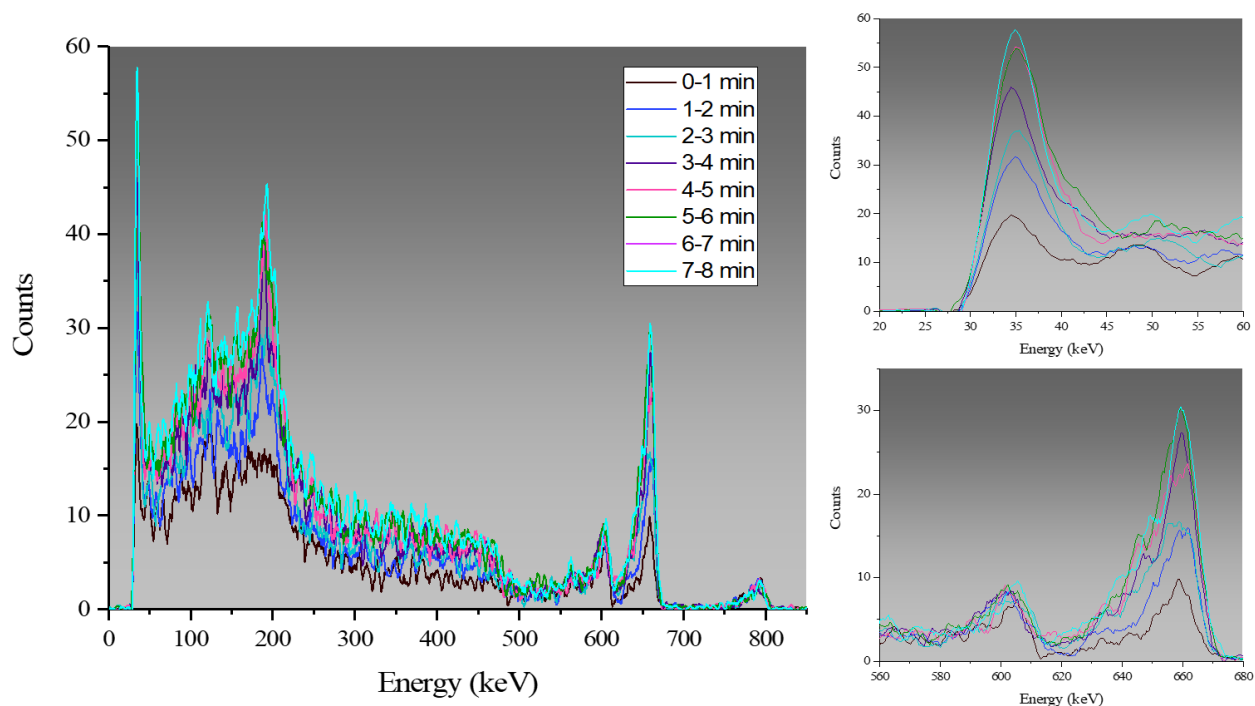


Figure 65. Illustration of barium ingrowth in the cesium spectra over eight one-minute counts. Upper-right plot shows the ^{137}Cs x-ray in better detail, while the lower-right plot shows the ^{137}Cs 662-keV peak.

The resulting spectra were plotted together to better observe the barium ingrowth as a function of time after the cesium/barium separation (see Figure 65). It can be seen how the 662 keV (and corresponding x-ray at 32 keV) increase in counts over each minute from the previous minute, especially in the first few minutes. If additional measurements had been acquired, full attainment of secular equilibrium could have been observed; however, that would have required around 18 minutes, as that is the point where the barium theoretical ingrowth fraction became 99% of the initial cesium activity. Once again, the unique CZT peak tailing can be observed even with these short 1-min measurements.

Additionally, the features noted earlier for the cesium spectrum (Compton edge, plateau, and backscatter peak) can also be observed as growing in at the same rate as the 32 and 662 keV peaks,

further correlating them with ^{137}Cs , rather than ^{134}Cs . However, the two ^{134}Cs peaks (604 and 795 keV) can be seen as static as a function of time after separation, which is expected due to those gammas being emitted directly from cesium rather than a barium daughter.

7.3.3 Transient CZT Gamma Chromatograms

The next part of this inline CZT experiment involved obtaining a transient gamma chromatogram, which required a source with adequate activity to be observed by the CZT detector over background without stopping the HPIC pumps for additional dwell time. The second source selected for this work, the AW sample from the ORNL ^{238}Pu process, fulfilled this requirement (see section 5.4.1). To begin, a five-minute count of the unseparated sample was acquired with the CZT, shown in Figure 66, and notably, the dead time of the detector was 41.3% because of the sample's high gamma activity.

The correlating lack of resolution in the low-energy region (<150 keV) can be seen, which is most likely due to the phenomenon of pulse pile up (caused by the superposition of two pulses arriving at the same time in the detector) in tandem with the large amount of dead time. For example, since ^{144}Ce is the highest activity isotope in this sample (see Table 39), the respective gammas expected are: 41, 80, and 134 keV. However, if these gammas interacted with the CZT at the same time, the resulting summed “gammas” would register as 175 or 214 keV, which both fall within the largest peak visible in the spectrum shown in Figure 66 (instead of the expected gammas). Additionally, if two 134 keV gammas were super-positioned/summed, that would result in a peak at ~ 270 keV – a peak can be observed at this energy in the spectrum, and no other gamma emission is expected at that point at that magnitude (i.e. ^{154}Eu has a 247 keV peak but is three magnitudes lower activity in this sample). However, the two main peaks expected from ^{106}Ru (the second highest activity isotope in this sample) can be observed: 511 keV and 620 keV. There are a couple additional peaks

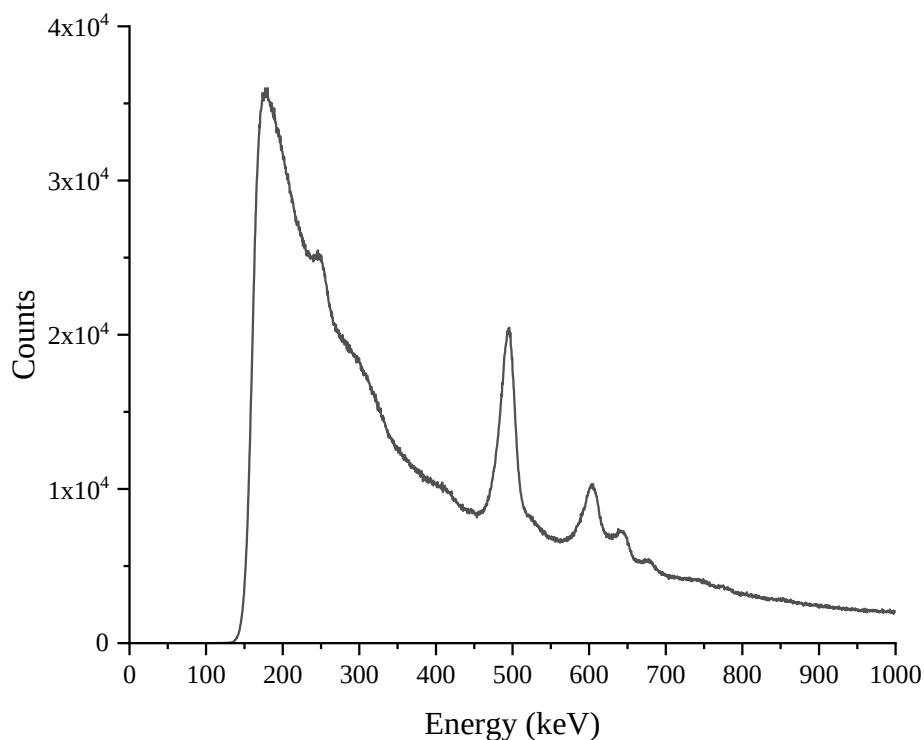


Figure 66. Five-minute count of the unseparated AW sample with the CZT detector.

visible in this spectrum, but they cannot be confidently identified with the unseparated sample (or at this dilution).

Next, an injection was performed to screen the sample and to verify the elution times of each element selected for analysis (ruthenium, cesium, cerium, europium, and americium) within the sample's neptunium matrix with the RAPID separation. Figure 67 illustrates the resulting separation with each peak labeled, including neodymium (for clarity), since the 144 m/z exists as both neodymium and cerium in this sample. Initially, it was discovered that the cerium was eluting twice, and that occurrence was attributed to the fact that cerium can exist in two oxidation states (+3, +4). Once 10 μ L of HAN (hydroxyl-ammonium nitrate) was added to the sample pre-injection, the majority of the cerium (~95%) eluted at once, instead of at two separate times,

showing that it was successfully reduced to its trivalent state that RAPID utilizes to separate lanthanides. This screen demonstrated the clear separation of each element of interest from each other, besides ruthenium and cesium, and set a precedence of when to expect each element post-injection at the CZT.

After this HPIC-ICPMS screen, three injections were performed with the sample while the CZT acquired data with the Lynx MSS mode at a rate of 30 s per spectrum. To better visualize the data after acquisition, each set of gamma spectra (approximately 60 spectra per separation) was loaded into GADRAS and observed with its time history function. The first separation's gamma chromatogram, illustrated by GADRAS, is displayed in Figure 68, with the peaks labeled using the known elution times from the ICPMS chromatogram in Figure 67. It can be seen that the americium was not at a high enough activity to be seen transiently (its activity is the lowest of the isotopes given in Table 39), however, the other isotopes were. To illustrate the consistency between injections, Figure 69 shows all three gamma chromatograms as generated in GADRAS – the peak shapes differ slightly but the elution times and durations are approximately the same. This demonstrates the repeatability of this method from a gamma detection perspective.

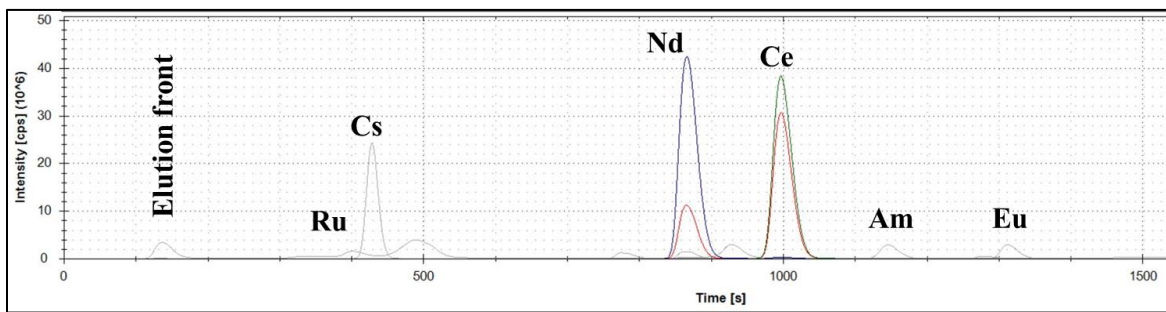


Figure 67. Mass chromatogram of an injection of AW to assess elution times of expected radioactive fission products (Nd shown for clarity).

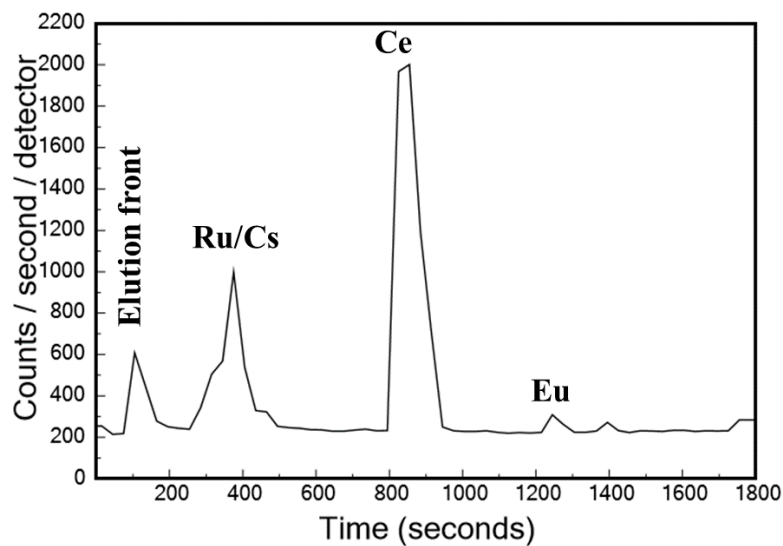


Figure 68. Gamma chromatogram of an injection of AW as illustrated in GADRAS with the peaks labeled for comparison to the mass chromatogram.

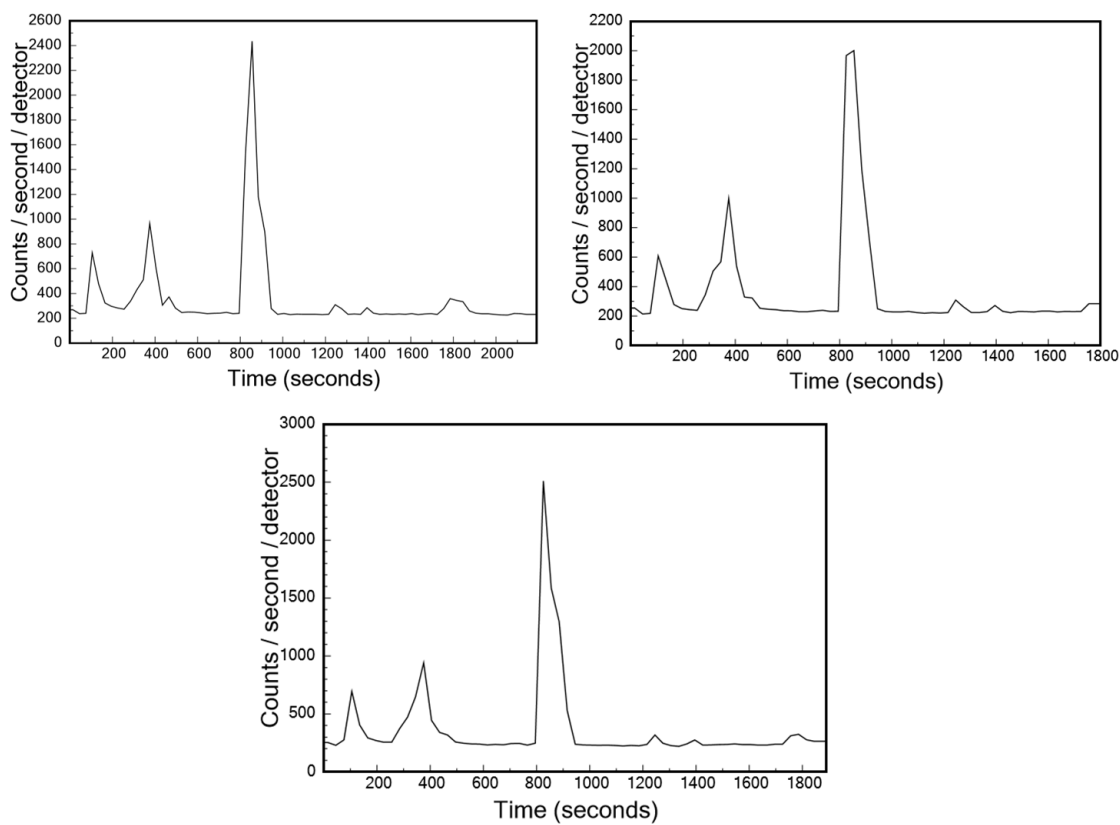


Figure 69. Gamma chromatograms of all three injections of AW visualized in GADRAS to show consistency of elution times.

To verify the identity of each spectra, and to view as a function of gamma energy rather than time, GADAS was used to select the activity peak of interest (foreground) and a background (see Figure 70), and from this, a background-subtracted gamma spectrum for each element/elution time was generated. Table 41 lists the correlating gammas and x-rays from each of the isotopes expected in the sample. However, as described earlier, both ^{106}Ru and ^{137}Cs are beta-emitters that are chemically separated from the isotopes generating their signature gammas (^{106}Rh and $^{137\text{m}}\text{Ba}$), so those gammas are not expected to be seen in the post-separation CZT spectra.

Using GADRAS, csv files were generated for each peak (ruthenium/cesium, cerium, and europium) for each of the triplicate runs to visualize using ORIGIN and its data smoothing filters. Figures 71–73 illustrate the resulting spectra for each peak with all three replicates overlaid with MCNP results.

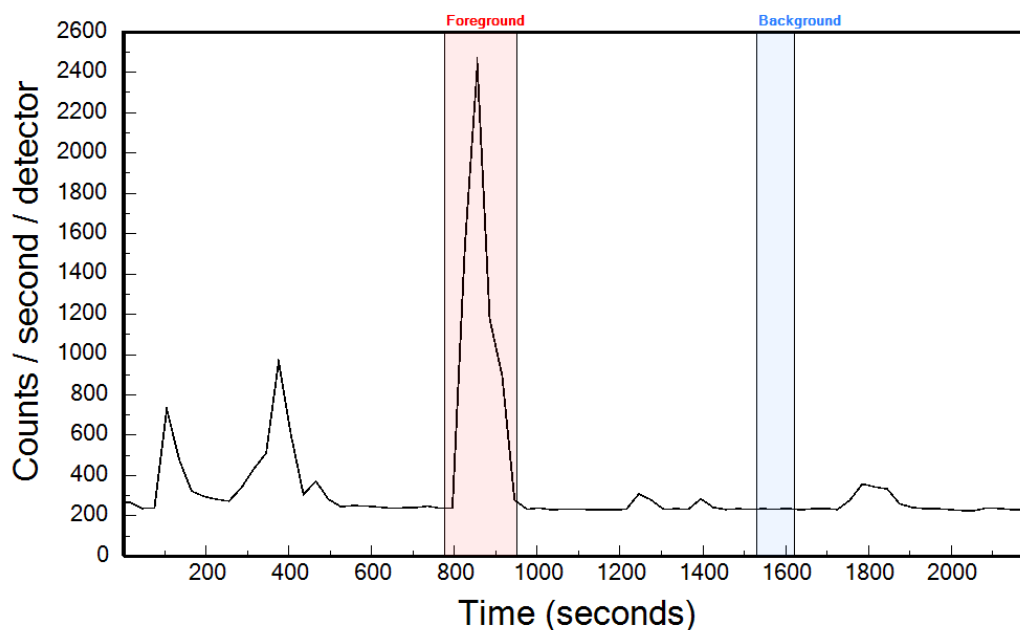


Figure 70. Illustration of background subtraction in GADRAS to acquire CZT spectra as a function of energy.

Table 41. Gammas and x-rays characteristic of the radioactive isotopes in the AW sample.

Isotope	γ (keV)		Isotope	γ (keV)
^{103}Ru	20.2		^{141}Ce	145.4
	53.3		^{144}Ce	36.0
	497.1			80.1
	610.3			133.5
^{106}Rh	511.9		^{154}Eu	43.0
	621.9			123.1
^{134}Cs	475.4		^{155}Eu	86.5
	563.2			105.3
	569.3		^{243}Am	43.5
	604.7			74.7
$^{137\text{m}}\text{Ba}$	661.7			117.6

First, the cesium and ruthenium fraction had two main peaks in addition to some low-energy noise. From the activity calculations in section 7.2, it is known that the ratio of ^{103}Ru : ^{134}Cs in this injection is ~ 6 , so it can be expected that the ruthenium is more prominently seen in the spectra than the cesium. Both of the peaks can be attributed to ruthenium (497 and 610 keV), and the Compton edge from ruthenium's 497 keV peak (338 keV) can even be seen in these low-count spectra. Also, as seen in the simulated spectrum, there is a small peak around ~ 50 keV that correlates to the 53 keV from ^{103}Ru and can be seen in the CZT data as well, at the forefront of the noisy low-energy peak area. There is also some noise in the low-energy region from ~ 50 – 200 keV that is not predicted in the simulated spectrum (seen in red), so it may be a feature caused by another radioisotope which is separated at the same time as ruthenium and cesium, but not anticipated in this study. Other possibilities are a backscatter peak, as in the previous section, at 200 keV, and x-rays from shielding material (such as lead x-rays around 78–87 keV) typically exist in that energy region. Of note, the MCNP spectrum is presented on a log scale to better view the peaks.

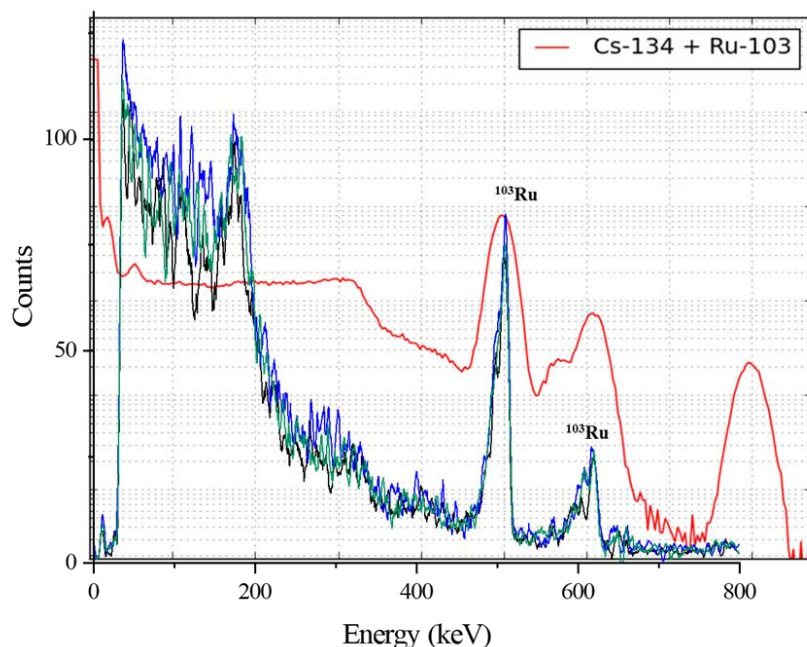


Figure 71. Smoothed, background-subtracted (through GADRAS) Ru spectra from triplicate acquisitions with the CZT, summed from $t = 250\text{--}430$ s in Figure 61. Overlaid (in red) is the summed ruthenium-cesium MCNP simulated spectrum.

Next, the cerium fraction can be easily identified as such with very characteristic peaks. Each one of ^{144}Ce 's peaks can be seen in these spectra – x-rays at ~ 35 keV, and the two gammas at 80 and 134 keV. Since the ratio of $^{144}\text{Ce}:$ ^{141}Ce is over 100, the contribution from ^{141}Ce was expected to be minimal, but the peak at 145 keV can be seen on the side of the 134 keV peak. As expected from the initial screening, the activity is highest from this fraction, and the peak heights reflect that, as the 134 keV peak (11% intensity) reaches a height of over 2000 in a 30 s long acquisition compared to the previous (ruthenium) spectra, which barely hit 100 counts of peak height. It should be noted that the MCNP simulated spectra is presented in conjunction with this CZT data to compare peak location/shape, and the height of its peaks is negligible (since it is simulated as a probability). Regardless, the simulated and experimental spectra match well, except for the small 145 keV peak from ^{141}Ce in the CZT data.

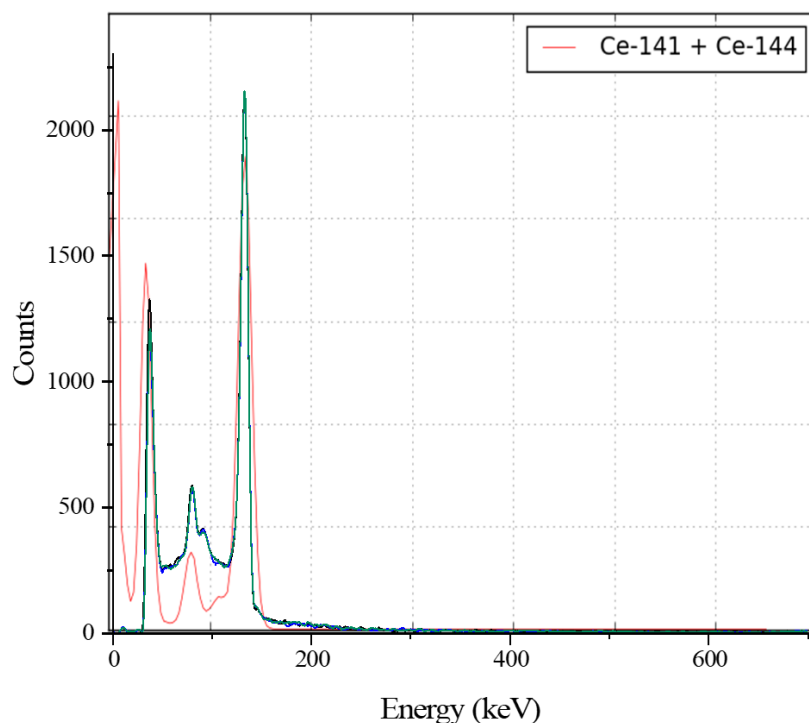


Figure 72. Smoothed, background-subtracted (through GADRAS) Ce spectra from triplicate acquisitions with the CZT, summed from $t = 780\text{--}960$ s in Figure 61. Overlaid (in red) is the summed ruthenium-cesium MCNP simulated spectrum.

Lastly, the europium fraction is presented below, and distinct peaks can be observed even with the very low count rates (europium had the lowest activity injected in this sample, three orders of magnitude lower than cerium). All four peaks listed in Table 41 can be visible – 43, 86, 105, and 123 keV from both isotopes of europium within the sample. As the activities injected from each of the isotopes are comparable (ratio was ~ 1), a near equal contribution was expected for this fraction. The MCNP spectra is overlaid on the CZT results, but in a position to compare peak energies and general spectral shape (i.e. that spectrum does not have negative counts). Obviously, the injected activity is barely (or at) background, but the energies of the peaks match the expected (and MCNP-predicted) peaks, which shows the additional sensitivity provided by the chemical separation pre-detection needed to observe these low-activity isotopes.

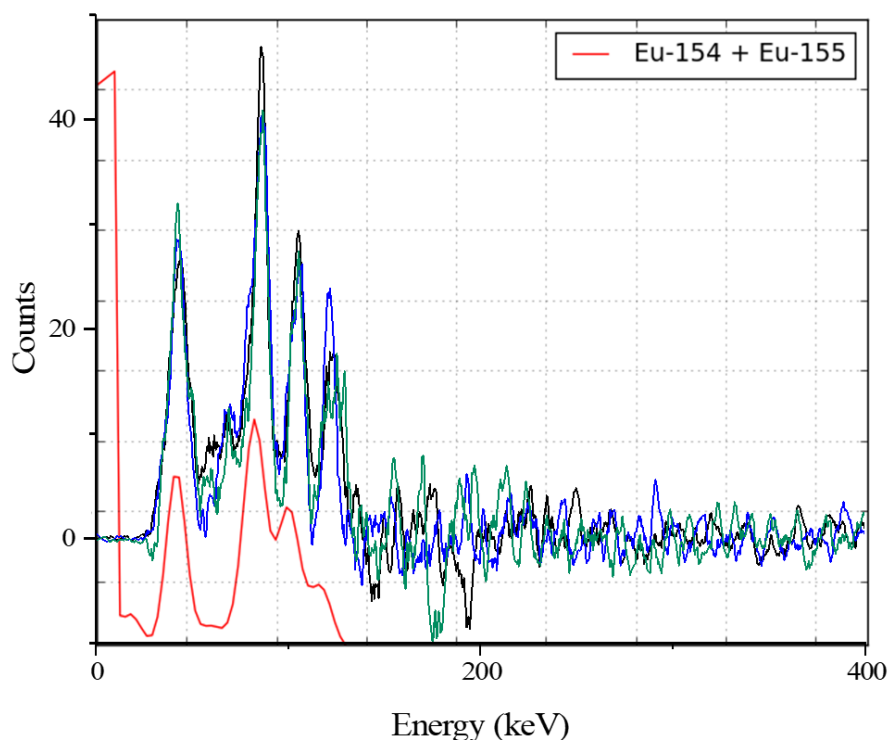


Figure 73. Smoothed, background-subtracted (through GADRAS) Eu spectra from triplicate acquisitions with the CZT, summed from $t = 1200\text{--}1290$ s in Figure 61. Overlaid (in red) is the summed ruthenium-cesium MCNP simulated spectrum.

7.3.4 Fraction Collection HPGe Measurements

To further verify the identity of ruthenium and europium in the CZT data (eluting at approximately 250–430 and 1200–1290 s, respectively), the fraction collector was used to collect those fractions for HPGe analysis. As seen in the previous section, peaks were harder to identify in those spectra due to their lower activities in the sample (compared to cerium). Once each fraction (one ruthenium and one europium) were collected, they were counted individually for approximately 30 minutes each with an HPGe. HPGe analysis is not typically performed after chemical separation, so this experiment demonstrated the utility of this “clean” gamma spectra (note that the dead time would be much higher with no separation). Figures 74–76 show the results from both the samples as

screenshots taken from PeakEasy software in log (to show full energy spectra) and linear (to more easily compare to the CZT spectra). Peaks are labeled within the software, identifying the ruthenium and europium in the samples.

To demonstrate the newfound sensitivity of the HGPGe on chemically separated samples, Table 42 provides a large list of the gammas emitted from ruthenium²¹⁶ (103 and 106 [technically emitted from ¹⁰⁶Rh]) and whether they were identified in the provided spectra.

Table 42. List of all gammas identified in the ruthenium HPGe spectrum post-separation.

¹⁰³ Ru			¹⁰⁶ Ru (¹⁰⁶ Rh)		
Energy (keV)	Intensity	ID?	Energy (keV)	Intensity	ID?
497.1	8.95E-01	✓	1988.4	2.58E-04	✓
610.3	5.64E-02	✓	1496.4	2.40E-04	✓
20.2	4.77E-02	-	434.2	2.00E-04	-
557	8.36E-03	✓	23.9	1.61E-04	-
53.3	3.76E-03	-	1927.2	1.47E-04	✓
¹⁰⁶ Ru (¹⁰⁶ Rh)			2406.0	1.45E-04	n/a
511.9	2.05E-01	✓	1180.8	1.44E-04	✓
621.9	9.87E-02	✓	1045.8	1.31E-04	-
1050.4	1.49E-02	✓	1114.5	1.17E-04	✓
616.2	7.31E-03	✓	439.2	1.11E-04	-
873.5	4.35E-03	✓	680.23	1.03E-04	-
1128.0	3.98E-03	✓	Unidentified peaks (keV)		
1562.2	1.56E-03	✓	176	Backscatter?	
428.5	7.04E-04	✓	463	¹²⁵ Sb	
21.2	5.86E-04	-	600	¹²⁵ Sb	
1194.6	5.73E-04	✓	607	¹²⁵ Sb	
2112.5	3.51E-04	n/a	635	¹²⁵ Sb	
21.0	3.10E-04	-	1134	None – maybe sum peak	
1062.1	3.04E-04	✓	1385	Sum peak?	
1766.2	3.00E-04	✓	1489	Sum peak?	
1797.0	2.74E-04	✓	2001	Sum peak?	

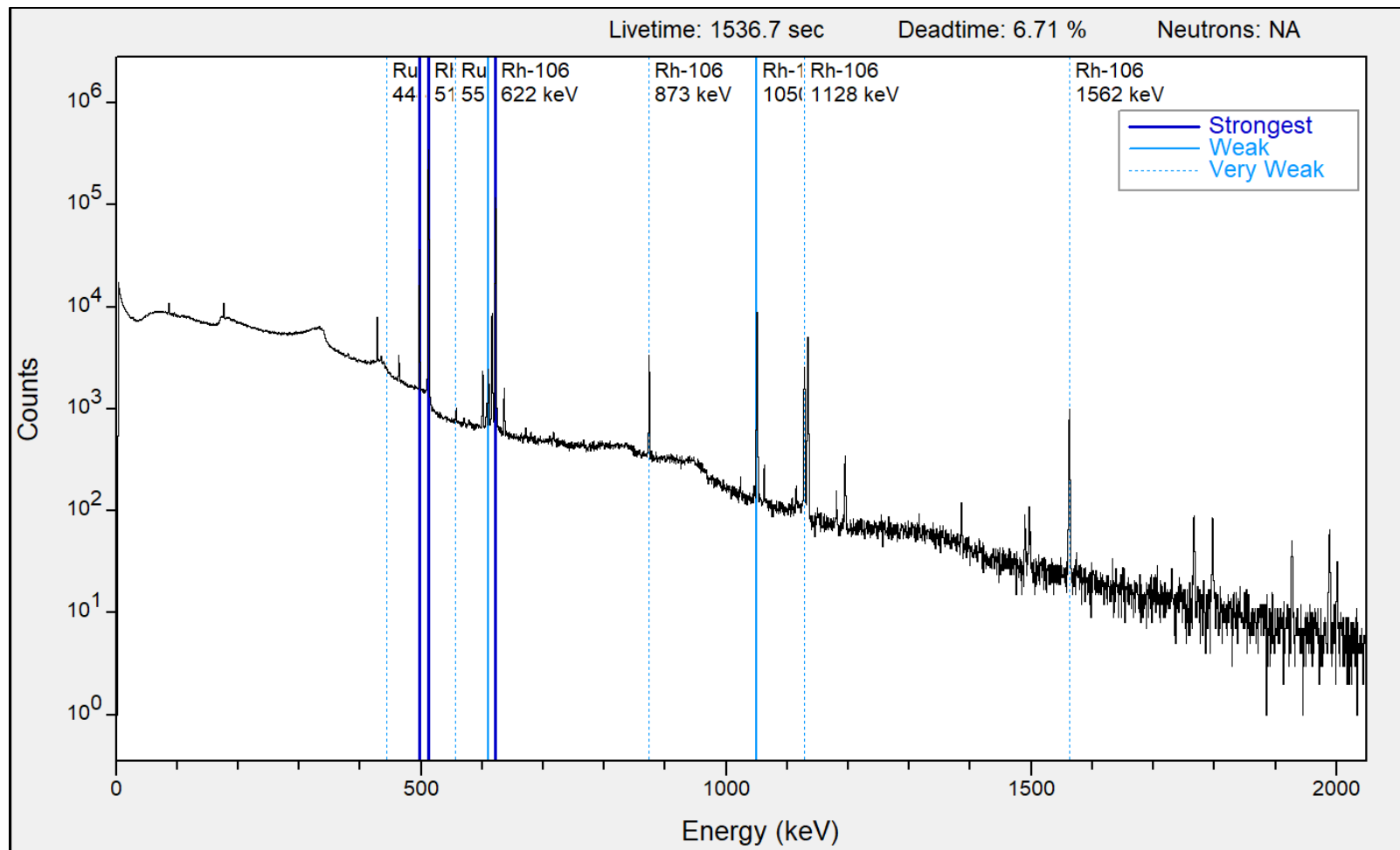


Figure 74. HPGe-acquired spectrum of the Ru fraction collected from the AW sample, displayed in log (counts). Major Ru peaks highlighted.

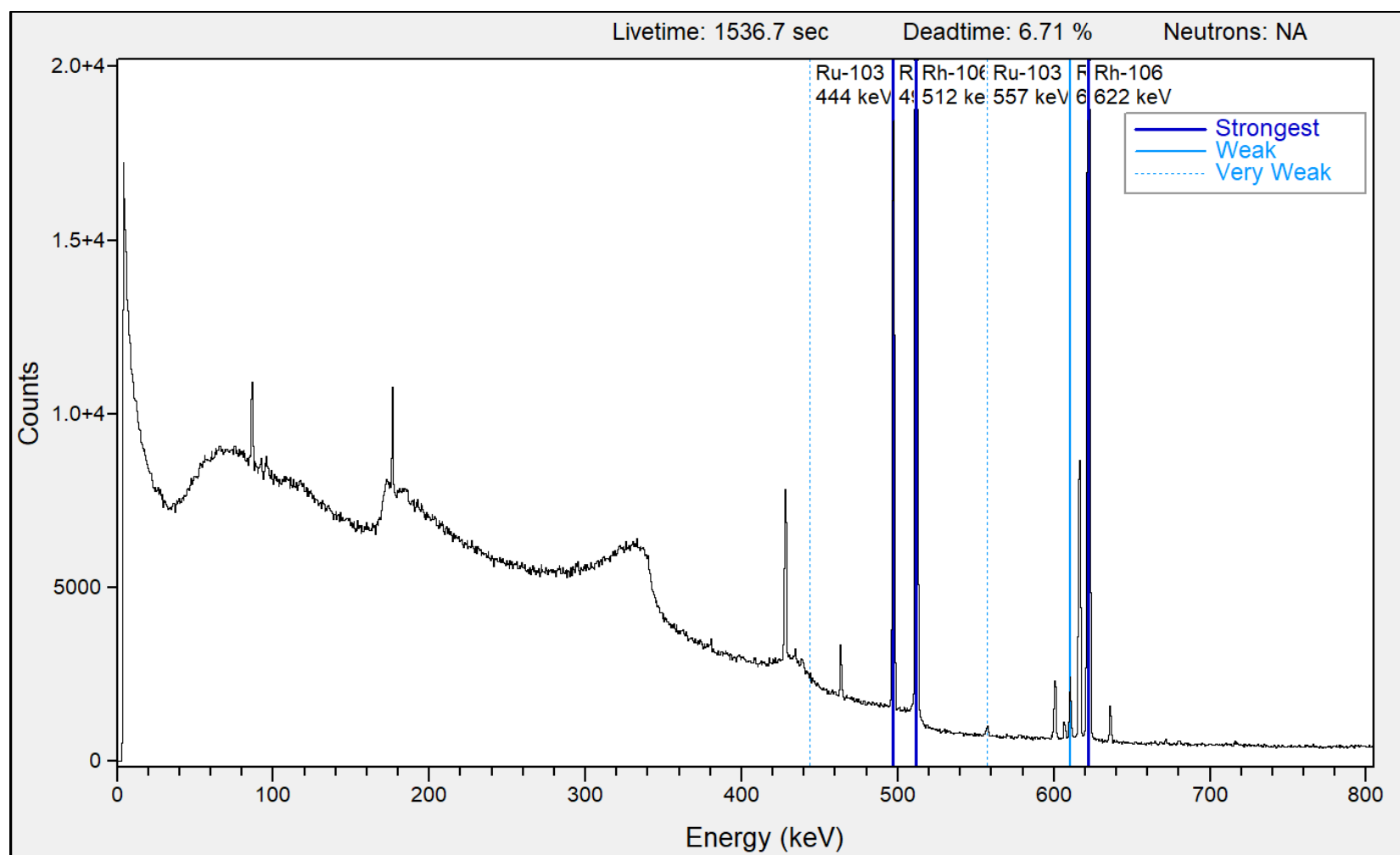


Figure 75. HPGe-acquired spectrum of the Ru fraction collected from the AW sample, displayed as linear (counts) to more easily compare to the CZT spectra. Major Ru peaks highlighted.

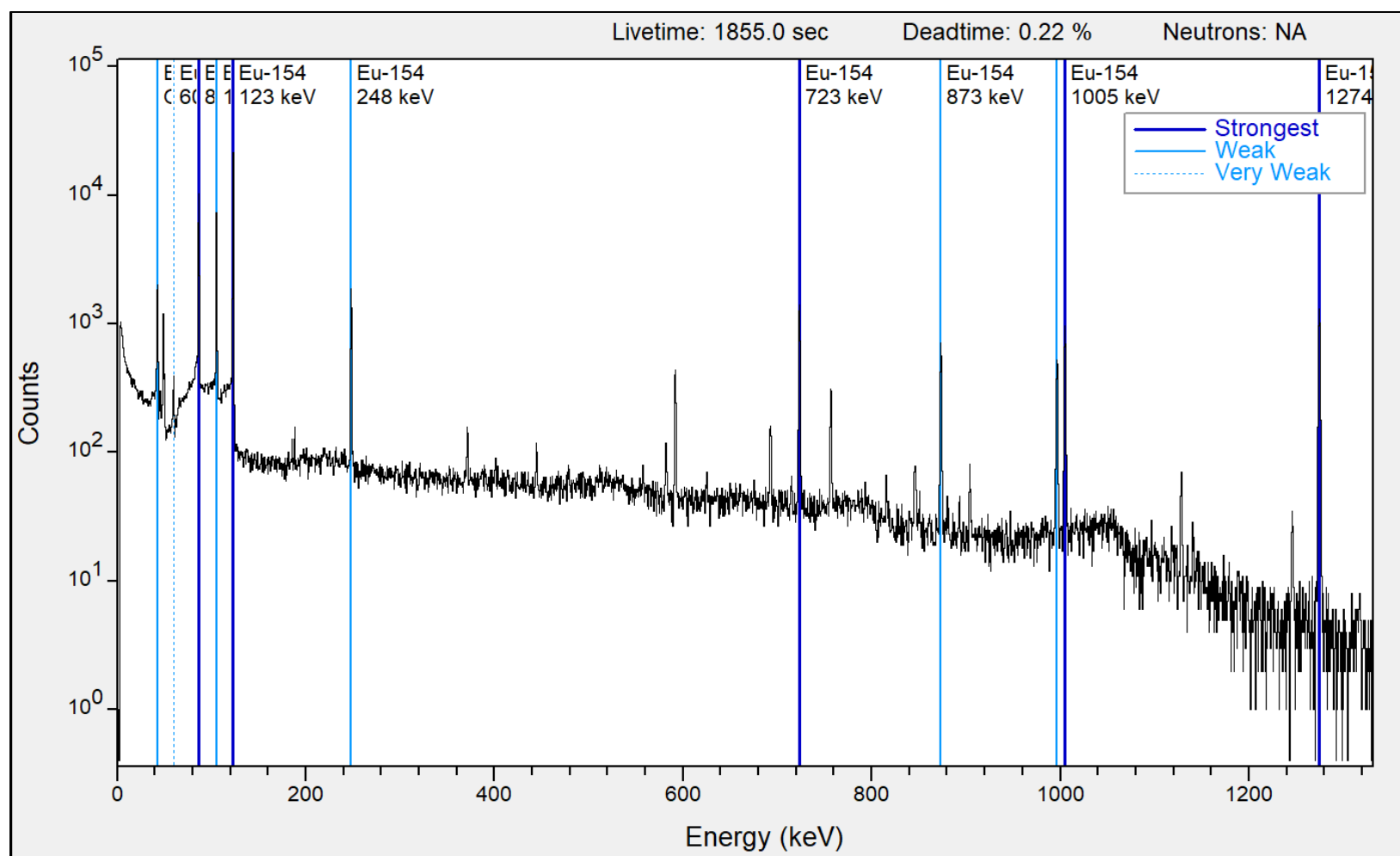


Figure 76. HPGe-acquired spectrum of the Eu fraction collected from the AW sample, displayed in log (counts). Eu peaks highlighted.

No cesium peaks were located in this spectrum – it is possible that the fraction was collected fairly cleanly (i.e. purely ruthenium) since the ^{137}Cs and ^{103}Ru were injected at comparable activity levels yet there is no 662 keV peak in this acquisition. Additionally, it can be seen that the HPGe is not as sensitive to the low-energy gammas (and x-rays) like the CZT is, as no x-rays were observed in the spectrum. Of note, the HPGe calibration was only good until 2000 keV, so no energies higher than that were observed in this measurement.

The fact that peaks of intensities of $\sim 1\text{E-}4$ (the peak at 1114 keV has a decay probability of 0.0001 per overall emission) could be identified shows the sensitivity of the HPGe coupled with a sample after chemical separation. Also given in Table 41 are the list of observable peaks that are not identified as ruthenium – a peak search tool²¹⁶ was used to suggest isotopes for these gamma emissions, and they were filtered by half-life (for rational probability of existing within the sample). 90+% of the recommended isotopes for those peaks had half-lives ranging from ms to one or two days, which would not fit the irradiation and decay profile of this sample, thus they were not considered. The only isotope that was not eliminated and had multiple matches was ^{125}Sb , which is a fission product, however, it has not been extensively studied with RAPID, so its elution parameters for this particular separation scheme is unknown. The other unidentified peaks may be sum peaks, where two gammas interact with the detector at the exact same time and become incorrectly summed together to form a high-energy peak.

Following the same process as the ruthenium fraction, the europium fraction was assessed for as many peaks of ^{154}Eu and ^{155}Eu as were observed, given in Table 43 (spectrum show in Figure 76). Nearly every peak seen in the spectrum was identified as europium, even down to an intensity of $\sim 1\text{E-}3$, and two x-rays (43 and 48 keV) were visible in this spectrum, unlike the previous ruthenium HPGe spectrum. Thus, this is essentially a pure fission-generated europium gamma spectrum,

which is a unique capability. The unidentified peaks had no qualifying isotopes for these energies that fit the criteria of having half-lives longer than one day, so they are most likely sum peaks (i.e. $.123 \text{ keV} + 247 \text{ keV} = 370 \text{ keV}$). This reiterates the fact that this is a pure spectrum with no other contaminants or isotopes in it, which could provide a new capability to the assessment of fission-generated (and radioactive) elements for either nuclear forensics or a field such as NAA or some more basic science research (confirming modeling software, understand cross sections, etc.).

Table 43. List of all gammas identified in the europium HPGe spectrum post-separation.

¹⁵⁴ Eu			¹⁵⁵ Eu		
Energy (keV)	Intensity	ID?	Energy (keV)	Intensity	ID?
123.0706	4.04E-01	✓	86.5479	3.07E-01	✓
1274.429	3.49E-01	✓	105.3083	2.11E-01	✓
723.3014	2.01E-01	✓	42.9967	1.21E-01	✓
1004.718	1.79E-01	✓	6.73255	7.50E-02	-
42.9967	1.30E-01	✓	42.3093	6.70E-02	✓
873.1834	1.22E-01	✓	48.7687	3.84E-02	✓
996.25	1.05E-01	✓	45.299	1.31E-02	-
6.73255	7.10E-02	-	60.0086	1.22E-02	✓
247.9288	6.89E-02	✓	50.093	9.77E-03	-
591.755	4.95E-02	✓	26.531	3.16E-03	-
756.802	4.53E-02	✓	86.0591	1.54E-03	✓
48.7687	4.10E-02	✓	57.989	6.70E-04	-
692.4205	1.79E-02	✓	146.071	5.10E-04	-
1596.48	1.78E-02	✓	18.763	4.80E-04	-
50.093	1.08E-02	-	31.444	7.10E-05	-
904.064	8.90E-03	✓	10.4183	3.50E-05	-
582.01	8.86E-03	✓	21.035	4.60E-06	-
1246.121	8.62E-03	✓	Unidentified peaks (keV)		
1494.048	6.98E-03	✓			
845.416	5.86E-03	✓	371	Sum peak	
444.4924	5.60E-03	✓	1397	Sum peak?	
892.775	5.14E-03	✓	1719	Sum peak?	
815.53	5.12E-03	✓			
1128.552	3.17E-03	✓			
625.2556	3.17E-03	✓			
557.58	2.67E-03	✓			

CHAPTER 8: CONCLUSION

8.1 Research Highlights and Conclusions

This work has shown the development of a rapid separation-detection technique and application to the analysis of fission elements, which is an important analytical capability to the nuclear forensics community for the purpose of post-detonation debris analysis. This rapid chemical analysis technique (each separation is performed < 1 h) was developed based on previous work in the literature but expanded to include a larger suite of fission elements analyzed in one separation with lower limits of detection. Once developed, it was tested against several types of complex matrices, including surrogate and NIST-certified soil, and two separate surrogate post-detonation debris samples (composed of mostly silica), to ensure its robustness to matrix effects while maintaining good chemical separation and detection limits. After development, RAPID was used to analyze three irradiated uranium samples soon after irradiation at the ORNL HFIR facility, which allowed for a relatively quick transition from the reactor facility to the appropriate building on the ORNL campus. During these analyses, it was proven that RAPID can accurately match the fission product inventories predicted by a depletion software, ORIGEN (which utilized the exact flux and irradiation parameters of the HFIR facility), to within 1–2%. A number of these fission products were injected at the femtogram level, and RAPID still matched the ORIGEN predictions, further demonstrating the utility of RAPID to trace-level fission product analyses. However, during these analyses, it was realized that some fission products should be analyzed with gamma spectroscopy (and existed at levels below RAPID's detection limits), and an inline gamma detection system was designed and tested with another fission product sample from the ORNL campus. This inline gamma detection system, post-separation, pre-ICPMS and currently using a

CZT detector, has shown the capability to provide clean, elementally isolated gamma spectra, an accomplishment not yet published in the literature.

The combination of rapid chemical analysis using an ICPMS and an inline gamma detector immediately after separation can provide an accurate, quick screen of a large number of fission products soon after irradiation, which is a capability very applicable to the nuclear forensics post-detonation community.

8.2 Publication Highlights

The first paper¹⁹⁸ (Journal of Chromatography A, 2018) summarized efforts on RAPID's method development, where the concentration and isotopic composition of 48 elements in a single (<1 h separation) analysis were obtained. There is flexibility to either focus on lower uncertainty measurements using RAPID or IDMS of specific analytes or to provide a quick screen measuring the concentration of a large number of elements in a short period of time. Using the combination of RAPID and IDMS, measurements of lanthanide concentrations were attained with as low as 1% uncertainty. Additionally, the robustness of the method was tested with a surrogate soil sample, showing no change in sensitivity and detection limits (still in the low-picogram range). The trace lanthanide concentrations of a NIST-certified soil were measured with RAPID and IDMS, matching the certificate values well and showing the fast analysis process: the sample was spiked, dissolved, analyzed, and processed in under 12 h (for two replicates, one would take only 8 h).

The second paper²⁰⁸ (JRNC, 2019) was the first to show analysis of irradiated HEU with RAPID, comparing the results to ORIGEN to validate the accuracy of the technique. It focused on the analysis of fission-generated, non-natural isotopes in a uranium matrix post-irradiation. Ratios of these non-natural isotopes were then compared to the predicted ORIGEN values, and a difference

of ~1–2% was observed, even with some of the isotopes existing at a femtogram level in the analysis. These results emphasize the accuracy, low detection limits, and high robustness to a uranium matrix that RAPID can provide to the nuclear forensics community (and others).

Next, the third paper²¹² (Talanta, 2019) built on the second paper by showing additional analysis of HEU fission products and comparison to ORIGEN, however, the turnaround from irradiation to analysis was much quicker, and some of the fission products were observed in their medium-lived decays/ingrowth. Fission products with half-lives ~33 h (and longer) were measured at 178 h after irradiation with a 1–2% difference from the predicted isotopic composition by ORIGEN. Additional measurements were performed with offline ICPMS and HPGe to confirm some of the RAPID measurements. It was discovered (through poor recovery of mass compared to that in ORIGEN) that the fission products were embedding themselves deep within the irradiation ampoule, and thus the leach was not fully recovering all fission products. This observation will lead to the use of a more aggressive dissolution procedure for the next target.

Lastly, the fourth paper²¹⁴ (JRNC, 2020) discussed the method development of the inline CZT detector, the acquisition of “gamma chromatograms”, which are gamma spectra as a function of time, and the subsequent HPGe analysis of the separated fractions from a RAPID separation. A mix of medium- and long-lived fission products from two irradiated samples (nuclear fuel and ²³⁸Pu process waste) were chemically separated with the HPIC and immediately analyzed with the CZT before detection by the ICPMS. Notably, ingrowth of the ^{137m}Ba daughter from ¹³⁷Cs was observed (half-life of 2.5 min), which could not be performed without an immediate detection capability after separation. To verify the composition of fission products, each sample was characterized before separation by RAPID and HPGe, and after separation, a fraction collector was used to generate fractions for analysis by HPGe post-separation for several elements. This test

demonstrated the additional capability that an inline gamma detector adds to the RAPID method, combining a gamma detection and mass spectrometry to fully characterize irradiated nuclear materials.

8.3 Lessons Learned – Applied Scenario

Through the development and assessment of the RAPID protocol as it pertains to nuclear forensics, several lessons were learned that will be useful given a real post-detonation analysis scenario. These lessons will be given through example, as if ORNL were sent a sample, and the US government needed results as soon as possible.

First, both ICPMS and gamma spectrometry are necessary analytical techniques for full characterization of the sample's fission products: a non-destructive HPGe screen would be the first step (time dependent on activity of sample), followed by a microwave dissolution as preparation for ICPMS analysis (~2 h). Once the sample was digested (fully or partially, depending on the glass formation in the sample), RAPID's HPIC-ICPMS protocol will be used to screen the sample (1 h). However, it is highly possible that the levels of fission products existing within the sample will be below the detection limits of the ICPMS. If that is the case, the fraction collector will be utilized to collect all elements post-separation (1–2 h) and analyzed with an MC-ICPMS (< 1 h) and an HPGe (1–2 h). Additionally, an inline gamma detector (ideally HPGe) can be used to screen for the gamma-emitting fission products that may be getting swamped by short-lived fission products in the HPGe analysis (1 h). This process is illustrated in Figure 77, from receipt of sample through all the various analyses possible and their associated timeframes.

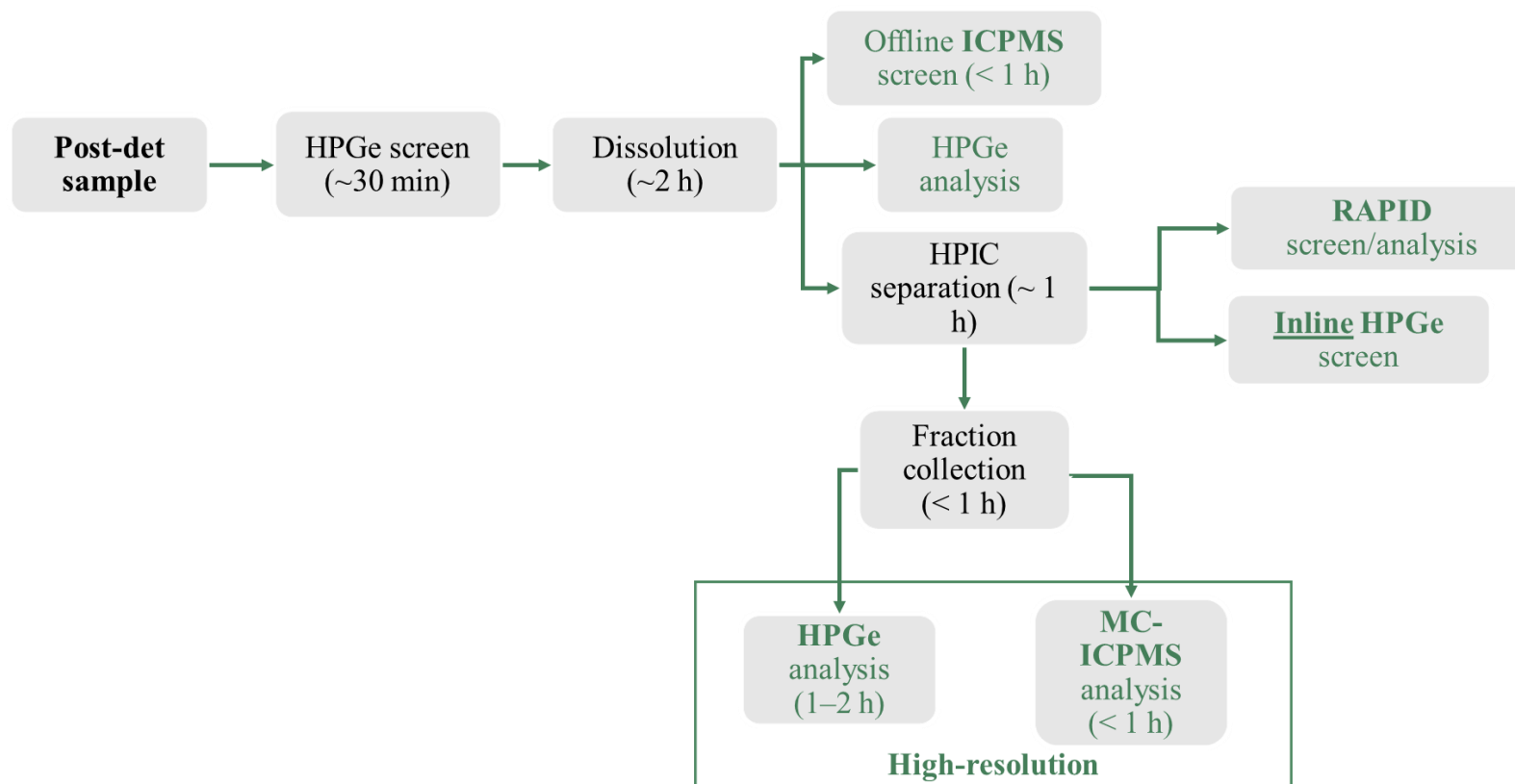


Figure 77. A diagram illustrating the rapid analytical process (and subsequent timeframes) that could be performed at ORNL for a post-detonation sample with RAPID and an updated inline HPGe detector. Green font correlates with an instrument providing a set of data for the sample.

These complementary acquisition methods of chemical separation, mass spectrometry, and gamma spectroscopy can provide a full fission product characterization of the sample within 24 h of receipt.

8.4 Areas of Continuation

Future work includes performing inline gamma tests with samples under the RAPID detection limits to quantify isotopic activity (which can be back calculated to mass) and better understand the limitations of both techniques and how the two complement each other.

Secondly, the goal is to replace the inline CZT with a mechanically-cooled HPGe and begin quantification of transient gamma signals after characterizing the efficiency of the sample loop configuration with known standards/samples. Eventually, to bolster the NAA capability at ORNL, it would be ideal to install an HPIC and inline HPGe in the NAA lab at HFIR to rapidly analyze short-lived fission products immediately after irradiation and separation from known gamma interferences (e.g. activation of elements not being analyzed). In this situation, it would be useful to develop a peak identification software in python which analyzes the inline HPGe data real-time, which would provide quicker results and a more effective analysis than is currently being done.

Lastly, RAPID will continue to be utilized as necessary for any NACIL projects, such as used nuclear fuel, REDC products, and more.

CHAPTER 9: FUTURE WORK

This section will walk through the final experiment that would have been performed if HFIR's irradiation schedule had not changed midway through this PhD project. The process will be similar to that presented in Figure 77, but with current capabilities (i.e. inline CZT instead of inline HPGe). The experiment will be presented in the form of an analytical chemistry procedure and includes an approach to the data analysis and relevant questions to ask about the results.

SCOPE:

To rapidly characterize the resulting fission products of an irradiated ^{239}Pu target with multiple techniques, including gamma spectroscopy, chemical separation, and mass spectrometry, and to compare these results to predicted fission products using the ORIGEN depletion code.

Additionally, to simulate post-detonation debris, an aliquot of the irradiated sample will be doped with an ORNL-developed surrogate matrix and taken through the same analytical process and compared to the undoped results.

APPARATUS:

- Analytical balance
- Pipets
- 20 μL syringe
- High-purity silica ampoules
- Heat lamp
- Sample vials
- Milestone microwave
- HPGe gamma detector

- RAPID equipment (HPIC, inline CZT, iCAP-Q ICPMS)
- Multi-collector ICPMS

REAGENTS & MATERIALS:

- DI water
- Trace-metals grade nitric acid
- Inorganic Ventures 71A, B, C, and D standards
- IRMM-86 (^{239}Pu standard)
- HPIC eluents (see section 4.3.1)
- ORNL-generated surrogate debris (dissolved)

PREPARATION OF APPARATUS

- Perform daily pipet and balance checks
- See section 4.3.2 for preparation of the ICPMS and HPIC system

PROCEDURE

- 1) Prepare plutonium targets for irradiation in HFIR NAA PT-1
 - a. Using the syringe, pipet 20 μL of the IRMM-86 into each silica ampoule
 - b. Position the heat lamp over the ampoules and use until solution has dried within each ampoule
 - c. Repeat a-b for a total of ~ 40 μL total IRMM-86 in each ampoule (~ 55 μg ^{239}Pu)
 - d. Seal the ampoules to NAA standards (i.e. no holes and length < 18 mm)
- 2) Analyze IRMM-86 solution with RAPID
 - a. 10 μL IRMM-86 in 1 mL 8M nitric acid
 - i. Dilute by 10x with DI water before injection

- ii. Triplicate injections with RAPID
- b. 10 μL IRMM-86 in 1 mL ORNL debris post-dissolution ($\sim 8\text{M}$ nitric)
 - i. Dilute by 10x with DI water before injection
- 3) Generate ORIGEN model with the plutonium target information
 - a. 54.131 μg ^{239}Pu
 - b. 1.6818 ng ^{238}Pu
 - c. 1.2151 μg ^{240}Pu
 - d. 13.46 ng ^{241}Pu
 - e. 4.1004 ng ^{242}Pu
 - f. Irradiation time: 1 h
 - g. HFIR flux: measured on the day of irradiation
- 4) Irradiate the plutonium targets in HFIR NAA PT-1 for 1 h (generating $\sim 1.7\text{E}14$ fissions)
 - a. Coordinate with NAA RCTs to transfer irradiated targets as soon as possible based on dose rates
- 5) Leach/dissolve the targets
 - a. Crush ampoule as described in section 6.3.3 then transfer to microwave vessel
 - b. Add any additional acid ($\sim 5\text{ mL}$ 8M nitric) to vessel before running dissolution protocol
- 6) Prepare aliquots for analysis
 - a. HPGe (scintillation vial) – 100 μL in 10 mL DI water (100x)
 - i. Dilution is dependent on gamma activity, modify as necessary
 - b. Offline ICPMS – 5-10x using DI water
 - c. RAPID – perform the smallest dilution possible (at least a 2x to dilute acid)

- i. Without additional matrix: dilute with DI water in autosampler vial (1.5 mL)
- ii. With matrix: dilute with DI water and surrogate debris solution in autosampler vial (1.5 mL)
- iii. For fraction collection:
 - 1. Spike one aliquot with 20-ppb 71ABCD in autosampler vial
 - 2. Second aliquot: dilute 2x in DI water

7) Analyze HPGe aliquot

- a. Depending on activity of the aliquot, count long enough to generate >10k counts in each peak of interest
 - i. Additional dilutions may need to be performed if dead time prevents analysis of certain fission products (i.e. ^{137}Cs – 662 keV gamma)

8) Analyze offline ICPMS aliquot

- a. Fission product screen/scan of the aliquot

9) Analyze aliquots with RAPID – full 52-min separation (see Table 10)

- a. Aliquot without matrix in triplicate
 - i. Bracket each injection with a blank and/or HCl injection
 - ii. Bracket triplicate set with 10-ppb 71ABCD injections for mass bias/calibration
 - iii. Inline CZT data acquisition for each injection (30 s spectra with MSS mode)
- b. Aliquot with matrix in triplicate
 - i. Bracket each injection with a blank and/or HCl injection
 - ii. Bracket triplicate set with 10-ppb 71ABCD injections

- iii. Inline CZT data acquisition for each injection (30 s spectra with MSS mode)
- c. Fraction collection aliquot – *this will be done based on any analytical gaps from the RAPID measurements, so the initial data analysis must be completed on the RAPID data before this step can be taken*
 - i. Are there isotopes below the detection limits of RAPID's MS analysis that need to be analyzed with a higher sensitivity machine?
 - 1. If so, collect these fractions for MC-ICPMS analysis
 - a. Spike aliquot with a known amount of natural standard before RAPID separation to observe the appropriate elution times
 - 2. If a higher precision analysis is required for any specific elements, design an appropriate IDMS experiment and implement at this step, spiking before separating with RAPID and fraction collection
 - ii. Are there any additional radioactive isotopes that registered with the inline CZT that were not accounted for with the initial HPGe screen?
 - 1. If so, fraction collect the correlating fractions to count on the HPGe post-separation using the same method of spiking a natural standard into the aliquot before injection and separation

10) Analyze fractions with HPGe

- a. Dilute fraction(s) into 10 mL using DI water
- b. Count the fractions as long as necessary to generate >10k counts in each major peak

11) Analyze fractions with MC-ICPMS

- a. Dilute as necessary for analysis

- i. If the fraction is too dilute, the sample may be dried on a hot plate to concentrate it and reconstituted in a smaller volume of nitric/DI water
 - b. If IDMS was determined to be required for select elements, follow the appropriate IDMS procedure (see section 3.2.5.3)
 - c. Analyze natural standards (71ABCD) for mass bias and external calibration
- 12) Update ORIGEN model to account for exact analysis times as necessary after irradiation for each set of analyses
- a. Generate masses and isotopic composition of fission products expected at each time

CALCULATIONS

- 1) Calculate the natural contamination in IRMM-86 material using external calibration
 - a. With and without the added ORNL surrogate matrix
 - i. What contamination may be in a real post-detonation sample that could interfere with the analysis?
- 2) Generate a list of fission product masses with ORIGEN corresponding to each analysis (input each time after irradiation in the ORIGEN input deck under “decay”)
 - a. Initial HPGe screen
 - b. Offline ICPMS screen
 - c. RAPID injections
 - i. Additionally, generate atom percent values of each isotope with ORIGEN
 - d. Fraction-collected HPGe analyses
 - e. Fraction-collected MC-ICPMS analyses
 - i. Add ORIGEN atom percent values for each isotope selected for analysis

- 3) For all HPGe data, use the Genie2K software to calculate isotopic masses for every radioactive fission product measured
 - a. Uncertainties provided within Genie2K report
- 4) For the offline ICPMS screen, no specific isotopic mass calculations will be performed due to the multitude of isobaric interferences, rather the screen will be used to compare to ORIGEN's predicted fission product curve (generate figure similar to Figure 51)
- 5) For the RAPID results:
 - a. Calculate mass bias from the 71ABCD injections (see section 3.2.5)
 - b. Calculate the concentrations of all isotopes observed over background using the 71ABCD standard as an external calibration standard
 - i. Blank subtract and correct for mass bias (refer again to section 3.2.5)
 1. For the surrogate matrix-doped analyses, subtract the matrix contributions (if any) for relevant peaks
 - ii. Calculate isotopic composition of each fission element
 - iii. Calculate uncertainty using the instrumental precision for each set of measurements and propagated as described in section 3.4
 - iv. Compare the resulting masses and compositions to ORIGEN
 1. Are the "recoveries" any different for the matrix-doped aliquot?
 2. Did the dissolution get a better recovery (per total mass of each isotope) than the previous leach (section 6.4.3)?
 - v. Compare the resulting masses to the initial HPGe data – do they match?

1. What data can be obtained with the HPGe that can't be acquired with RAPID (i.e. falls under detection limits or is not separated well with the HPIC)?
 - vi. Analyze the gamma chromatograms generated by the inline CZT detector
 1. Are there any additional radioactive isotopes that registered with the CZT that were not accounted for with the initial HPGe screen?
 - vii. Compare the overall fission product curve (two hump curve) with the one generated for HEU (Figure 51)
 1. Are there any differences?
 - a. Calculate various isotopic ratios to compare the HEU and Pu fission products and compare to the ORIGEN-predicted values
 - b. Is RAPID sensitive enough to distinguish between fission products generated with HEU and Pu?
- 6) If the MC-ICPMS was used:
- a. Calculate the concentration/isotopic composition of the selected elements
 - i. Blank subtract and correct for mass bias
 - ii. Calculate uncertainty by utilizing instrumental precision and appropriate uncertainty propagation
 - b. Compare to ORIGEN-predicted values
 - i. If there are any elements analyzed with both RAPID and the MC-ICPMS, is there any notable difference in the recoveries from ORIGEN?

- c. If IDMS was performed, complete the corresponding calculations as described in section 3.2.5 to calculate the elemental concentration and associated isotopic composition of each selected element
 - i. Follow the uncertainty calculations described in section 3.2.5

INTERPRETATION OF RESULTS

Since there are no actual results for this experiment, this section will hypothesize answers to some of the questions posed in the calculations section.

In section 3.4 of this dissertation, complex matrices (with associated contamination that would be comparable to that of a real post-detonation sample) were used for IDMS and detection limit measurements, and the results were only slightly affected. Ideally, the matrix would be completely removed from the sample before analysis, however, realistically, especially in a necessarily rapid analysis, there needs to be an awareness of what matrix contamination could entail (if no matrix blanks are provided), so it can be accounted for.

In the comparison between the doped and undoped (with surrogate debris) fission product aliquots, the effect of a matrix may be seen, though the method development results (chapter 5) imply otherwise – the addition of a matrix should not affect RAPID’s results if the matrix blank is used to correct the results before comparison. This will further prove RAPID’s robustness to matrices while maintaining accuracy and precision during fission product analyses.

The use of a full dissolution to leach the generated, energetic fission products from the walls of the silica ampoules will be useful to inform any further experiments performed this way. If the recovery is still not ideal, a change in irradiation method may be required while maintaining the requirements by HFIR (fission products must be in a sealed container as to not release gaseous

fission products). A potential method could involve loading of the sample onto an aluminum or titanium (easily dissolvable) backing then sealed within the silica ampoule.

Previous work (section 6.3.3.2) utilized both RAPID and HPGe to characterize HEU fission products, and the results matched, thus it is expected that this remains the case with this irradiated plutonium sample. Additionally, the results from the initial HPGe screen can be used to predict what the inline CZT detector may see in tandem with the ORIGEN predictions (in the case of radioactive isotopes generated but not seen with the HPGe screen before separation). If the CZT does register these additional radioactive isotopes that the HPGe did not, and they are not analyzed with RAPID (due to detection limits or current separation capability), then the addition of this capability provides the opportunity to fully characterize these fission products over a short period of time in such a way that was not possible before.

Next, the most important question from a nuclear forensics perspective: *does RAPID have the sensitivity to distinguish between fission products resulting from irradiation of HEU compared to ^{239}Pu ?*

Figure 78 illustrates the predicted difference in the fission product curves from these two materials (with the same irradiation conditions in HFIR). It can be seen that there is a notable shift between the two curves, however, is it measurable using a rapid analytical screen in less than an hour (or <4–5 h including HPGe/MC-ICPMS)? To test this, once the fission products from the irradiated plutonium target are analyzed with RAPID+ (including HPGe and MC-ICPMS), various ratios of the fission products can be calculated and compared between data sets. For example, using the ORIGEN data, the ratio of mass 103 to 140 is 0.35 for HEU and 0.95 for ^{239}Pu – what do the results from RAPID give (within uncertainties)? Further utilizing ORIGEN, more specific ratios can be calculated for both HEU and ^{239}Pu fission products at exact decay times after irradiation to

compare RAPID results to. Once this data is collected and thoroughly assessed, this question can be answered.

Lastly, if the MC-ICPMS is used to analyze some of these fission products, how does it compare to the values predicted by ORIGEN (does it have a better recovery than RAPID by itself)? Theoretically, the answer is yes, as the MC-ICPMS can attain high precision in its analysis.

Ideally, the MC-ICPMS can be complementarily used to RAPID for a more thorough fission product characterization – most notably by measuring some of the fission products that fall below RAPID’s detection limits, such as europium and gadolinium. Measuring a ratio between masses 98 and 158 (or perhaps 99 and 106) gives a large difference between HEU and ^{239}Pu , with ratios of 1170 and 72, respectively. If the MC-ICPMS can be used in tandem with the RAPID separation to analyze this ratio (and others with similarly large discrepancies), a difference between HEU and ^{239}Pu should be determined.

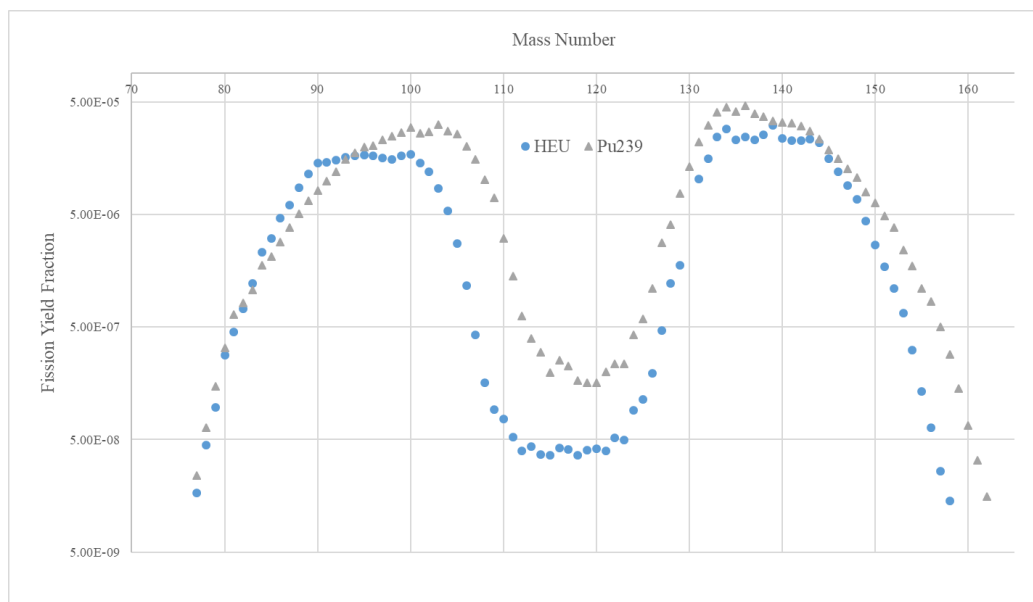


Figure 78. The fission yield curves calculated through ORIGEN for an HEU target (blue circles) compared to a ^{239}Pu target (gray triangles).

REFERENCES

- (1) Qaim, S. M. Radiochemical Determination of Nuclear Data for Theory and Applications. *J. Radioanal. Nucl. Chem.* **2010**, 284 (3), 489–505. <https://doi.org/10.1007/s10967-010-0460-5>.
- (2) Schwantes, J.; Marsden, O.; Pellegrini, K. State of Practice and Emerging Application of Analytical Techniques of Nuclear Forensic Analysis: Highlights from the 4th Collaborative Materials Exercise of the Nuclear Forensics International Technical Working Group {(ITWG)}. *J Radioanal Nucl Ch* **2016**, 311 (2), 1–12. <https://doi.org/10.1007/s10967-016-5037-5>.
- (3) Fahey, A.; Zeissler, C.; Newbury, D.; Davis, J.; Lindstrom, R. Postdetonation Nuclear Debris for Attribution. *Proc Natl. Acad Sci* **2010**, 107 (47), 20207–20212. <https://doi.org/10.1073/pnas.1010631107>.
- (4) Tan, S. H.; Horlick, G. Matrix Effect Observations in ICPMS. *J. Anal. At. Spectrom.* **1987**, 2 (December), 745–763.
- (5) Kim, Y.; Kawaguchi, H.; Tanaka, T.; Mizuike, A. Non-Spectroscopic Matrix Interferences in Inductively Coupled Plasma- Mass Spectrometry Analyte Signals as Well as on Its Applications to Inorganic Trace Analysis . The Analyte Signals in ICP-MS Are Influenced Not Only by the Operating Parameters of the I. *Spectrochimica Acta* **1990**, 458 (3), 333–339.
- (6) Agatemor, C.; Beauchemin, D. Matrix Effects in Inductively Coupled Plasma Mass Spectrometry: A Review. *Anal. Chim. Acta* **2011**, 706, 66–83. <https://doi.org/10.1016/j.aca.2011.08.027>.
- (7) Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons, 2006.
- (8) Roach, B. D.; Hexel, C. R.; Giaquinto, J. M. ORNL TM-2017-694: *Demonstration of a Rapid HPLC-ICPMS Direct Coupling Technique Using IDMS Project Report Part I*; 2017.
- (9) Molgaard, J.; Auxier, J.; Giminaro, A.; Oldham, C.; Cook, M.; Young, S.; Hall, H. Development of Synthetic Nuclear Melt Glass for Forensic Analysis. *J Radioanal Nucl Ch* **2015**, 304 (3), 1293–1301. <https://doi.org/10.1007/s10967-015-3941-8>.
- (10) Nizinski, C.; Giminaro, A.; Auxier, J.; Cook, M.; Hall, H. Production and Characterization of Synthetic Urban Nuclear Melt Glass. *J Radioanal Nucl Ch* **2017**, 314 (3), 2349–2355. <https://doi.org/10.1007/s10967-017-5522-5>.

- (11) Giminaro, A. V.; Stratz, S. A.; Gill, J. A.; Auxier, J. P.; Oldham, C. J.; Cook, M. T.; Auxier II, J. D.; Molgaard, J. J.; Hall, H. L. Compositional Planning for Development of Synthetic Urban Nuclear Melt Glass. *Under Rev. J.Rad.Nucl.Chem.*
- (12) Fedchenko, V. The Role of Nuclear Forensics in Nuclear Security. *Strateg. Anal.* **2014**, 38 (2), 230–247. <https://doi.org/10.1080/09700161.2014.884442>.
- (13) Song, K.; Park, J.-H.; Lee, C.-G.; Han, S.-H. Recent Developments in Nuclear Forensic and Nuclear Safeguards Analysis Using Mass Spectrometry. *Mass Spectrom Lett* **2016**, 7 (2), 31–40. <https://doi.org/10.5478/MSL.2016.7.2.31>.
- (14) Stratz, S. A.; Gill, J. A.; Auxier II, J. D.; Hall, H. L. Modern Advancements in Post-Detonation Nuclear Forensic Analysis Modern Advancements in Post-Detonation Nuclear Forensic Analysis Modern Advancements in Post-Detonation Nuclear Forensic Analysis. *Int. J. Nucl. Secur.* **2016**, 2 (3). <https://doi.org/10.7290/V7W37T8H>.
- (15) Carney, K.; Finck, M.; Christopher, M.; Martin, L.; Lewis, R. The Development of Radioactive Glass Surrogates for Fallout Debris. *J Radioanal Nucl Ch* **2014**, 299 (1), 363–372. <https://doi.org/10.1007/s10967-013-2800-8>.
- (16) Bellucci, J. J.; Simonetti, A.; Koeman, E. C.; Wallace, C.; Burns, P. C. A Detailed Geochemical Investigation of Post-Nuclear Detonation Trinitite Glass at High Spatial Resolution: Delineating Anthropogenic vs. Natural Components. *Chem. Geol.* **2014**, 365, 69–86. <https://doi.org/10.1016/j.chemgeo.2013.12.001>.
- (17) Sharp, N.; William, M.; Ticknor, B.; Ash, R.; Piccoli, P.; Borg, D. Rapid Analysis of Trinitite with Nuclear Forensic Applications for Post-Detonation Material Analyses. *J Radioanal Nucl Ch* **2014**, 302 (1), 57–67. <https://doi.org/10.1007/s10967-014-3285-9>.
- (18) Lewis, L. A.; Knight, K. B.; Matzel, J. E.; Prussin, S. G.; Zimmer, M. M.; Kinman, W. S.; Ryerson, F. J.; Hutcheon, I. D. Spatially-Resolved Analyses of Aerodynamic Fallout from a Uranium-Fueled Nuclear Test. *J Env. Radioact.* **2015**, 148, 183–195. <https://doi.org/10.1016/j.jenvrad.2015.04.006>.

- (19) Bellucci, J.; Simonetti, A.; Wallace, C.; Koeman, E.; Burns, P. Isotopic Fingerprinting of the World's First Nuclear Device Using Post-Detonation Materials. *Anal Chem* **2013**, 85 (8), 4195–4198. <https://doi.org/10.1021/ac400577p>.
- (20) Roman, A. R.; Bond, E. M. A New Method for Separating First Row Transition Metals and Actinides from Synthetic Melt Glass. *J. Radioanal. Nucl. Chem.* **2016**, 307 (3), 2471–2478. <https://doi.org/10.1007/s10967-016-4695-7>.
- (21) Bonamici, C. E.; Kinman, W. S.; Fournelle, J. H.; Zimmer, M. M.; Pollington, A. D.; Rector, K. D. A Geochemical Approach to Constraining the Formation of Glassy Fallout Debris from Nuclear Tests. *Contrib. to Mineral. Petrol.* **2017**, 172 (1). <https://doi.org/10.1007/s00410-016-1320-2>.
- (22) Wallace, C.; Bellucci, J.; Simonetti, A.; Hainley, T.; Koeman, E.; Burns, P. A Multi-Method Approach for Determination of Radionuclide Distribution in Trinitite. *J Radioanal Nucl Ch* **2013**. <https://doi.org/10.1007/s10967-013-2497-8>.
- (23) Hanson, S.; Pollington, A.; Waidmann, C.; Kinman, W.; Wende, A.; Miller, J.; Berger, J.; Oldham, W.; Selby, H. Measurements of Extinct Fission Products in Nuclear Bomb Debris: Determination of the Yield of the Trinity Nuclear Test 70 y Later. *Proc Natl. Acad Sci* **2016**, 113 (29), 8104–8108. <https://doi.org/10.1073/pnas.1602792113>.
- (24) Jonkmans, G.; Anghel, V. N. P.; Jewett, C.; Thompson, M. Nuclear Waste Imaging and Spent Fuel Verification by Muon Tomography. *Ann. Nucl. Energy* **2013**, 53, 267–273. <https://doi.org/10.1016/j.anucene.2012.09.011>.
- (25) Lantzios, I.; Kouvalaki, C.; Nicolaou, G. Plutonium Fingerprinting in Nuclear Forensics of Spent Nuclear Fuel. *Prog. Nucl. Energy* **2015**, 85, 333–336. <https://doi.org/10.1016/j.pnucene.2015.07.002>.
- (26) JOE, K.; HAN, S.-H.; SONG, B.-C.; LEE, C.-H.; HA, Y.-K.; SONG, K. Inductively Coupled Plasma Mass Spectrometry for the Determination of ²³⁷Np in Spent Nuclear Fuel Samples by Isotope Dilution Method Using ²³⁹Np as a Spike. *Nucl. Eng. Technol.* **2013**, 45 (3), 415–420. <https://doi.org/10.5516/NET.06.2012.056>.

- (27) Alonso, J. I. G.; Sena, F.; Arbore, P.; Betti, M.; Koch, L.; Alonso, I. J.; Sena, F.; Arbore, P.; Betti, M.; Koch, L. Determination of Fission Products and Actinides in Spent Nuclear Fuels by Isotope Dilution Ion Chromatography Inductively Coupled Plasma Mass Spectrometry. *J. Anal. At. Spectrom.* **1995**, *10* (5), 381. <https://doi.org/10.1039/ja9951000381>.
- (28) Alonso, J. I. Determination of Fission Products and Actinides by Inductively Coupled Plasma-Mass Spectrometry Using Isotope Dilution Analysis: A Study of Random and Systematic Errors. *Anal Chim Acta* **1995**, *312* (1), 57–78. [https://doi.org/10.1016/0003-2670\(95\)00199-A](https://doi.org/10.1016/0003-2670(95)00199-A).
- (29) Chartier, F.; Aubert, M.; Pilier, M. Determination of Am and Cm in Spent Nuclear Fuels by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry and Isotope Dilution Thermal Ionization Mass Spectrometry after Separation by High-Performance Liquid Chromatography. *Fresenius' J Anal Chem* **1999**, *364* (4), 320–327. <https://doi.org/10.1007/s002160051343>.
- (30) Betti, M. Use of Ion Chromatography for the Determination of Fission Products and Actinides in Nuclear Applications. *J Chromatogr A* **1997**, *789* (1–2), 369–379. [https://doi.org/10.1016/S0021-9673\(97\)00784-X](https://doi.org/10.1016/S0021-9673(97)00784-X).
- (31) Betti, M.; Menichetti, L.; Moreno, J. M.; Fuoco, R. A Preliminary Study for the Determination of Long-Lived Radionuclides (Second Transition Group 4-d) in Environmental Samples by Ion Chromatography Inductively Coupled Plasma-Mass Spectrometry (IC-ICP-MS). *Microchem J* **2000**, *67* (1–3), 285–290. [https://doi.org/10.1016/S0026-265X\(00\)00074-6](https://doi.org/10.1016/S0026-265X(00)00074-6).
- (32) Keegan, E.; Kristo, M. J.; Colella, M.; Robel, M.; Williams, R.; Lindvall, R.; Eppich, G.; Roberts, S.; Borg, L.; Gaffney, A.; et al. Nuclear Forensic Analysis of an Unknown Uranium Ore Concentrate Sample Seized in a Criminal Investigation in Australia. *Forensic Sci Int* **2014**, *240*, 111–121. <https://doi.org/10.1016/j.forsciint.2014.04.004>.
- (33) Montgomery, J.; Jeffery, R. Asymmetrical Fission Products <http://www.unclear2nuclear.com/asymFission.php>.
- (34) Smith, D. K.; Kristo, M. J.; Niemeyer, S.; Dudder, G. B. Documentation of a Model Action Plan to Deter Illicit Nuclear Trafficking. *J. Radioanal. Nucl. Chem.* **2008**, *276* (2), 415–419. <https://doi.org/10.1007/s10967-008-0520-2>.

- (35) Croudace, I. W.; Warwick, P. E.; Reading, D. G.; Russell, B. C. Recent Contributions to the Rapid Screening of Radionuclides in Emergency Responses and Nuclear Forensics. *Trac Trends Anal Chem* **2016**, *85*, 120–129. <https://doi.org/10.1016/j.trac.2016.05.007>.
- (36) IAEA. IAEA Nuclear Security Series #2-G, Rev.1. Nuclear Forensics in Support of Investigations. 2015.
- (37) Dustin, M.; Koeman, E.; Simonetti, A.; Torrano, Z.; Burns, P. Comparative Investigation between In Situ Laser Ablation Versus Bulk Sample (Solution Mode) Inductively Coupled Plasma Mass Spectrometry {(ICP-MS)} Analysis of Trinitite {Post-Detonation} Materials. *Appl Spectrosc* **2016**, *70* (9), 1446–1455. <https://doi.org/10.1177/0003702816662597>.
- (38) Bürger, S.; Riciputi, L. R. A Rapid Isotope Ratio Analysis Protocol for Nuclear Solid Materials Using Nano-Second Laser-Ablation Time-of-Flight {ICP-MS}. *J Env. Radioact.* **2009**, *100* (11), 970–976. <https://doi.org/10.1016/j.jenvrad.2009.07.009>.
- (39) Maxwell, S. L.; Culligan, B. K.; Jones, V. D.; Nichols, S. T.; Bernard, M. A.; Noyes, G. W. Determination of ²³⁷Np and Pu Isotopes in Large Soil Samples by Inductively Coupled Plasma Mass Spectrometry. *Anal. Chim. Acta* **2010**, *682* (1–2), 130–136. <https://doi.org/10.1016/j.aca.2010.10.001>.
- (40) Maxwell, S. L.; Culligan, B. K.; Kelsey-Wall, A.; Shaw, P. J.; Angel, K.-W.; Shaw, P. J. Rapid Radiochemical Method for Determination of Actinides in Emergency Concrete and Brick Samples. *Anal Chim Acta* **2011**, *701* (1), 112–118. <https://doi.org/10.1016/j.aca.2011.06.011>.
- (41) Maxwell, S.; Culligan, B.; Hutchison, J. Rapid Determination of Actinides in Asphalt Samples. *J Radioanal Nucl Ch* **2014**, *299* (3), 1891–1901. <https://doi.org/10.1007/s10967-013-2885-0>.
- (42) Maxwell, S.; Culligan, B.; Noyes, G. Rapid Separation Method for Actinides in Emergency Air Filter Samples. *Appl Radiat Isot.* **2010**, *68* (12), 2125–2131. <https://doi.org/10.1016/j.apradiso.2010.05.018>.
- (43) Maxwell, S. L.; Culligan, B.; Hutchison, J. B.; Utsey, R. C.; Sudowe, R.; R, McAlister, D. Rapid Method to Determine ⁸⁹Sr/⁹⁰Sr in Large Concrete Samples. *J Radioanal Nucl Ch* **2016**, *310* (1), 399–411. <https://doi.org/10.1007/s10967-016-4787-4>.

- (44) Maxwell, S. L.; Culligan, B.; Hutchison, J. B.; Utsey, R. C.; Sudowe, R.; McAlister, D. R. Rapid Method to Determine $^{89}/^{90}\text{Sr}$ in Steel Samples. *J. Radioanal. Nucl. Chem.* **2017**, *310* (1), 399–411. <https://doi.org/10.1007/s10967-017-5402-z>.
- (45) Yang, G.; Tazoe, H.; Yamada, M. Rapid Determination of ^{135}Cs and Precise $^{135}\text{Cs}/^{137}\text{Cs}$ Atomic Ratio in Environmental Samples by Single-Column Chromatography Coupled to Triple-Quadrupole Inductively Coupled Plasma-Mass Spectrometry. *Anal. Chim. Acta* **2016**, *908*, 177–184. <https://doi.org/10.1016/j.aca.2015.12.041>.
- (46) Yi, X.; Shi, Y.; Xu, J.; He, X.; Zhang, H.; Lin, J. Rapid Determination of ^{237}Np in Soil Samples by Multi-Collector Inductively-Coupled Plasma Mass Spectrometry and Gamma Spectrometry. *J Radioanal Nucl Ch* **2013**. <https://doi.org/10.1007/s10967-013-2677-6>.
- (47) Datta, A.; Sivaraman, N.; Srinivasan, T. G.; Vasudeva Rao, P. R.; Rao, P. Rapid Separation of Lanthanides and Actinides on Small Particle Based Reverse Phase Supports. *Radiochim. Acta* **2010**, *98* (5), 277–285. <https://doi.org/10.1524/ract.2010.1715>.
- (48) Schwantes, J. M.; Rundberg, R. S.; Taylor, W. A.; Vieira, D. J. Rapid , High-Purity , Lanthanide Separations Using HPLC. **2006**, *418*, 189–194. <https://doi.org/10.1016/j.jallcom.2005.08.110>.
- (49) Habibi, A.; Vivien, C.; Boulet, B.; Cossonnet, C.; Gurriaran, R.; Gleizes, M.; Cote, G.; Larivière, D. A Rapid Sequential Separation of Actinides and Radiostrontium Coupled to ICP-MS and Gas Proportional Counting. *J. Radioanal. Nucl. Chem.* **2016**, *310* (1), 217–227. <https://doi.org/10.1007/s10967-016-4834-1>.
- (50) Varga, Z.; Nicholl, A.; Wallenius, M.; Mayer, K. Plutonium Age Dating (Production Date Measurement) by Inductively Coupled Plasma Mass Spectrometry. *J Radioanal Nucl Ch* **2016**, *307* (3), 1919–1926. <https://doi.org/10.1007/s10967-015-4418-5>.
- (51) Miyamoto, Y.; Suzuki, D.; Esaka, F.; Magara, M. Accurate Purification Age Determination of Individual Uranium–Plutonium Mixed Particles. *Anal Bioanal Chem* **2015**, *407* (23), 7165–7173. <https://doi.org/10.1007/s00216-015-8880-2>.

- (52) Marin, R.; Sarkis, J.; Nascimento, M. The Use of LA-SF-ICP-MS for Nuclear Forensics Purposes: Uranium Isotope Ratio Analysis. *J Radioanal Nucl Ch* **2013**, 295 (1), 99–104. <https://doi.org/10.1007/s10967-012-1980-y>.
- (53) Meyers, L.; Stephen, L.; Stalcup, A.; Spitz, H. Uranium Isotopic Signatures Measured in Samples of Dirt Collected at Two Former Uranium Facilities. *J Radioanal Nucl Ch* **2014**, 301 (2), 307–313. <https://doi.org/10.1007/s10967-014-3187-x>.
- (54) Saha, A.; Deb, S. B.; Saxena, M. K. Determination of Trace Impurities in Advanced Metallic Nuclear Fuels by Inductively Coupled Plasma Time-of-Flight Mass Spectrometry (ICP-TOF-MS). *J Anal Atom Spectrom* **2016**, 31 (7), 1480–1489. <https://doi.org/10.1039/C6JA00138F>.
- (55) Shi, Y.; Collins, R.; Broome, C. Determination of Uranium, Thorium and Plutonium Isotopes by ICP-MS. *J Radioanal Nucl Ch* **2013**, 296 (1), 509–515. <https://doi.org/10.1007/s10967-012-2128-9>.
- (56) Esaka, F.; Suzuki, D.; Miyamoto, Y.; Magara, M. Plutonium Age Determination from $^{240}\text{Pu}/^{236}\text{U}$ Ratios in Individual Particles by ICP-MS without Prior Chemical Separation. *Microchem J* **2015**, 118, 69–72. <https://doi.org/10.1016/j.microc.2014.08.006>.
- (57) Esaka, F.; Yasuda, K.; Suzuki, D.; Miyamoto, Y.; Magara, M. Analysis of Plutonium Isotope Ratios Including $^{238}\text{Pu}/^{239}\text{Pu}$ in Individual U–Pu Mixed Oxide Particles by Means of a Combination of Alpha Spectrometry and ICP-MS. *Talanta* **2017**, 165, 122–127. <https://doi.org/10.1016/j.talanta.2016.12.041>.
- (58) Kurosaki, H.; Cadieux, J.; Clark, S. An Alternative Method for Chronometric Determinations Involving Curium. *J Anal Atom Spectrom* **2014**, 29 (12), 2419–2423. <https://doi.org/10.1039/C4JA00256C>.
- (59) Russell, B. C.; Croudace, I. W.; Warwick, P. E.; Milton, J. A. Determination of Precise $^{135}\text{Cs}/^{137}\text{Cs}$ Ratio in Environmental Samples Using Sector Field Inductively Coupled Plasma Mass Spectrometry. *Anal. Chem.* **2014**. <https://doi.org/10.1021/ac501894a>.
- (60) Bürger, S.; Boulyga, S. F.; Peñkin, M. V.; Bostick, D.; Jovanovic, S.; Lindvall, R.; Rasmussen, G.; Riciputi, L. Quantifying Multiple Trace Elements in Uranium Ore Concentrates: An Interlaboratory Comparison. *J Radioanal Nucl Ch* **2014**, 301 (3), 711–729. <https://doi.org/10.1007/s10967-014-3224-9>.

- (61) Godoy, M.; Godoy, J.; Roldão, L.; Tauhata, L. Determination of Total Content and Isotopic Compositions of Plutonium and Uranium in Environmental Samples for Safeguards Purposes by {ICP-QMS}. *J Env. Radioact.* **2009**, *100* (8), 613–625. <https://doi.org/10.1016/j.jenvrad.2009.04.012>.
- (62) Martinelli, R.; Hamilton, T.; Williams, R.; Kehl, S. Separation of Uranium and Plutonium Isotopes for Measurement by Multi Collector Inductively Coupled Plasma Mass Spectroscopy. *J Radioanal Nucl Ch* **2009**, *282* (2), 343–347. <https://doi.org/10.1007/s10967-009-0150-3>.
- (63) Rožmarić, M.; Ivšić, A. G.; Grahek, Ž. Determination of Uranium and Thorium in Complex Samples Using Chromatographic Separation, ICP-MS and Spectrophotometric Detection. *Talanta* **2009**, *80* (1), 352–362. <https://doi.org/10.1016/j.talanta.2009.06.078>.
- (64) Muramatsu, Y.; Hamilton, T.; Uchida, S.; Tagami, K.; Yoshida, S.; Robison, W. Measurement of $^{240}\text{Pu}/^{239}\text{Pu}$ Isotopic Ratios in Soils from the Marshall Islands Using ICP-MS. *Sci Total Env.* **2001**, *278* (1–3), 151–159. [https://doi.org/10.1016/S0048-9697\(01\)00644-1](https://doi.org/10.1016/S0048-9697(01)00644-1).
- (65) Cizdziel, J.; Ketterer, M.; Farmer, D.; Faller, S.; Hodge, V. ^{239} , ^{240} , ^{241}Pu Fingerprinting of Plutonium in Western US Soils Using ICPMS: Solution and Laser Ablation Measurements. *Anal Bioanal Chem* **2008**, *390* (2), 521–530. <https://doi.org/10.1007/s00216-007-1741-x>.
- (66) Ketterer, M.; Hafer, K.; Link, C.; Kolwaite, D.; Wilson, J.; Mietelski, J. Resolving Global versus Local/Regional Pu Sources in the Environment Using Sector ICP-MS. *J Anal Atom Spectrom* **2004**, *19* (2), 241–245. <https://doi.org/10.1039/B302903D>.
- (67) Hoffmann, D. L. ^{230}Th Isotope Measurements of Femtogram Quantities for U-Series Dating Using Multi Ion Counting (MIC) MC-ICPMS. *Int. J. Mass Spectrom.* **2008**, *275* (1–3), 75–79. <https://doi.org/10.1016/j.ijms.2008.05.033>.
- (68) Ines, Günther-Leopold; Kivel, N.; Waldis, J.; Wernli, B. Characterization of Nuclear Fuels by ICP Mass-Spectrometric Techniques. *Anal Bioanal Chem* **2008**, *390* (2), 503–510. <https://doi.org/10.1007/s00216-007-1644-x>.

- (69) Kim, C.-S.; Kim, C.-K.; Martin, P.; Sansone, U. Determination of Pu Isotope Concentrations and Isotope Ratio by Inductively Coupled Plasma Mass Spectrometry: A Review of Analytical Methodology. *J Anal Atom Spectrom* **2007**, 22 (7), 827–841. <https://doi.org/10.1039/B617568F>.
- (70) I., Günther-Leopold; Waldis, J.; Wernli, B.; Kopajtic, Z. Measurement of Plutonium Isotope Ratios in Nuclear Fuel Samples by HPLC-MC-ICP-MS. *Int J Mass Spectrom* **2005**, 242 (2–3), 197–202. <https://doi.org/10.1016/j.ijms.2004.11.007>.
- (71) Stefánka, Z.; Katona, R.; Varga, Z. Laser Ablation Assisted ICP-MS as a Tool for Rapid Categorization of Seized Uranium Oxide Materials Based on Isotopic Composition Determination. *J Anal Atom Spectrom* **2008**, 23 (7), 1030–1033. <https://doi.org/10.1039/B804199G>.
- (72) Varga, Z.; Surányi, G. Detection of Previous Neutron Irradiation and Reprocessing of Uranium Materials for Nuclear Forensic Purposes. *Appl Radiat Isot.* **2009**, 67 (4), 516–522. <https://doi.org/10.1016/j.apradiso.2008.12.006>.
- (73) Park, J.; Kim, T.; Lee, C.-G.; Lee, J.; Lim, S.; Han, S.; Song, K. Combinatory Use of Time-of-Flight Secondary Ion Mass Spectrometry (SIMS) and Sector-Field SIMS for Estimating Elemental and Isotopic Compositions of Nuclear Forensic Samples. *J Radioanal Nucl Ch* **2016**, 311 (2), 1–10. <https://doi.org/10.1007/s10967-016-5070-4>.
- (74) Hedberg, P. M. L.; Peres, P.; Fernandes, F.; Renaud, L. Multiple Ion Counting Measurement Strategies by SIMS – a Case Study from Nuclear Safeguards and Forensics. *J Anal Atom Spectrom* **2015**, 30 (12), 2516–2524. <https://doi.org/10.1039/C5JA00382B>.
- (75) Willingham, D.; Naes, B. E.; Burns, K. A.; Reid, B. D. Secondary Ion Mass Spectrometry Signatures for Verifying Declarations of Fissile-material Production. *Appl Radiat Isot.* **2015**, 97, 125–129. <https://doi.org/10.1016/j.apradiso.2014.12.015>.
- (76) Peres, P.; Hedberg, P.; Walton, S.; Montgomery, N.; Cliff, J.; Rabemananjara, F.; Schuhmacher, M. Nuclear Safeguards Applications Using LG-SIMS with Automated Screening Capabilities. *Surf Interface Anal* **2013**, 45 (1), 561–565. <https://doi.org/10.1002/sia.5015>.

- (77) Ranebo, Y.; Eriksson, M.; Tamborini, G.; Niagolova, N.; Bildstein, O.; Betti, M. The Use of SIMS and SEM for the Characterization of Individual Particles with a Matrix Originating from a Nuclear Weapon. *Microsc Microanal* **2007**, *13* (3), 179–190. <https://doi.org/10.1017/S1431927607070353>.
- (78) Tamborini, G. SIMS Analysis of Uranium and Actinides in Microparticles of Different Origin. *Microchim Acta* **2004**, *145* (1–4), 237–242. <https://doi.org/10.1007/s00604-003-0160-8>.
- (79) Betti, M.; Tamborini, G.; Koch, L. Use of Secondary Ion Mass Spectrometry in Nuclear Forensic Analysis for the Characterization of Plutonium and Highly Enriched Uranium Particles. *Anal Chem* **1999**, *71* (14), 2616–2622. <https://doi.org/10.1021/ac981184r>.
- (80) Tamborini, G.; Phinney, D.; Bildstein, O.; Betti, M. Oxygen Isotopic Measurements by Secondary Ion Mass Spectrometry in Uranium Oxide Microparticles: A Nuclear Forensic Diagnostic. *Anal Chem* **2002**, *74* (23), 6098–6101. <https://doi.org/10.1021/ac0259515>.
- (81) Aggarwal, S. K. Thermal Ionisation Mass Spectrometry (TIMS) in Nuclear Science and Technology – a Review. *Anal. Methods* **2016**, *8* (5), 942–957. <https://doi.org/10.1039/C5AY02816G>.
- (82) Wallenius, M.; Mayer, K. Age Determination of Plutonium Material in Nuclear Forensics by Thermal Ionisation Mass Spectrometry. *Fresenius' J Anal Chem* **2000**, *366* (3), 234–238. <https://doi.org/10.1007/s002160050046>.
- (83) Bürger, S.; Riciputi, L. R.; Turgeon, S.; Bostick, D.; E., M.; Lavelle, M.; McBay, E.; Lavelle, M. A High Efficiency Cavity Ion Source Using TIMS for Nuclear Forensic Analysis. *J Alloy Compd* **2007**, *444* (SPEC. ISS.), 660–662. <https://doi.org/10.1016/j.jallcom.2006.11.019>.
- (84) Bürger, S.; Riciputi, L. R.; Bostick, D. A.; Turgeon, S.; McBay, E. H.; Lavelle, M.; E.H., M.; Lavelle, M. Isotope Ratio Analysis of Actinides, Fission Products, and Geolocators by High-Efficiency Multi-Collector Thermal Ionization Mass Spectrometry. *Int J Mass Spectrom* **2009**, *286* (2–3), 70–82. <https://doi.org/10.1016/j.ijms.2009.06.010>.

- (85) Bürger, S.; Balsley, S. D.; Baumann, S.; Berger, J.; Boulyga, S. F.; Cunningham, J. A.; Kappel, S.; Koepf, A.; Poths, J. Uranium and Plutonium Analysis of Nuclear Material Samples by Multi-Collector Thermal Ionisation Mass Spectrometry: Quality Control, Measurement Uncertainty, and Metrological Traceability. *Int. J. Mass Spectrom.* **2012**, *311*, 40–50. <https://doi.org/10.1016/j.ijms.2011.11.016>.
- (86) Esaka, F.; Suzuki, D.; Magara, M. Identifying Uranium Particles Using Fission Tracks and Microsampling Individual Particles for Analysis Using Thermal Ionization Mass Spectrometry. *Anal Chem* **2015**, *87* (5), 3107–3113. <https://doi.org/10.1021/acs.analchem.5b00236>.
- (87) Dunne, J.; Richards, D.; Chen, H.-W. Procedures for Precise Measurements of $^{135}\text{Cs}/^{137}\text{Cs}$ Atom Ratios in Environmental Samples at Extreme Dynamic Ranges and Ultra-Trace Levels by Thermal Ionization Mass Spectrometry. *Talanta* **2017**, *174*, 347–356. <https://doi.org/10.1016/j.talanta.2017.06.033>.
- (88) Park, J.-H.; Choi, E.-J. Simultaneous Determination of the Quantity and Isotopic Ratios of Uranium in Individual Micro-Particles by Isotope Dilution Thermal Ionization Mass Spectrometry {(ID-TIMS)}. *Talanta* **2016**, *160*, 600–606. <https://doi.org/10.1016/j.talanta.2016.08.006>.
- (89) Sturm, M.; Richter, S.; Aregbe, Y.; Wellum, R.; Prohaska, T. Optimized Chemical Separation and Measurement by TE TIMS Using Carburized Filaments for Uranium Isotope Ratio Measurements Applied to Plutonium Chronometry. *Anal Chem* **2016**, *88* (12), 6223–6230. <https://doi.org/10.1021/acs.analchem.5b03852>.
- (90) Suzuki, D.; Esaka, F.; Miyamoto, Y.; Magara, M. Direct Isotope Ratio Analysis of Individual Uranium–Plutonium Mixed Particles with Various U/Pu Ratios by Thermal Ionization Mass Spectrometry. *Appl Radiat Isot.* **2015**, *96*, 52–56. <https://doi.org/10.1016/j.apradiso.2014.11.012>.
- (91) Shibahara, Y.; Kubota, T.; Fujii, T.; Fukutani, S.; Takamiya, K.; Konno, M.; Mizuno, S.; Yamana, H. Determination of Isotopic Ratios of Plutonium and Uranium in Soil Samples by Thermal Ionization Mass Spectrometry. *J. Radioanal. Nucl. Chem.* **2016**, *307* (3), 2281–2287. <https://doi.org/10.1007/s10967-015-4551-1>.
- (92) Varga, Z.; Wallenius, M.; Mayer, K. Origin Assessment of Uranium Ore Concentrates Based on Their Rare-Earth Elemental Impurity Pattern. *Radiochim Acta* **2010**, *98* (12), 771–778. <https://doi.org/10.1524/ract.2010.1777>.

- (93) Varga, Z.; Katona, R.; Stefánka, Z.; Wallenius, M.; Mayer, K.; Nicholl, A. Determination of Rare-Earth Elements in Uranium-Bearing Materials by Inductively Coupled Plasma Mass Spectrometry. *Talanta* **2010**, *80* (5), 1744–1749. <https://doi.org/10.1016/j.talanta.2009.10.018>.
- (94) Varga, Z.; Wallenius, M.; Mayer, K.; Hrncsek, E. Alternative Method for the Production Date Determination of Impure Uranium Ore Concentrate Samples. *J Radioanal Nucl Ch* **2011**, *290* (2), 485–492. <https://doi.org/10.1007/s10967-011-1233-5>.
- (95) Varga, Z.; Wallenius, M.; Mayer, K.; Keegan, E.; Millet, S. Application of Lead and Strontium Isotope Ratio Measurements for the Origin Assessment of Uranium Ore Concentrates. *Anal Chem* **2009**, *81* (20), 8327–8334. <https://doi.org/10.1021/ac901100e>.
- (96) Knight, A.; Eitrheim, E.; Nelson, A.; Nelson, S.; Schultz, M. A Simple-Rapid Method to Separate Uranium, Thorium, and Protactinium for U-Series Age-Dating of Materials. *J Env. Radioact.* **2014**, *134*, 66–74. <https://doi.org/10.1016/j.jenvrad.2014.02.010>.
- (97) Varga, Z.; Nicholl, A.; Wallenius, M.; Mayer, K. Remeasurement of ^{234}U Half-Life. *Anal Chem* **2016**, *88* (5), 2763–2769. <https://doi.org/10.1021/acs.analchem.5b04370>.
- (98) Sommers, J.; Cummings, D.; Giglio, J.; Carney, K. “Age” Determination of Irradiated Materials Utilizing Inductively Coupled Plasma Mass Spectrometric (ICP-MS) Detection. *J Radioanal Nucl Ch* **2009**, *282* (2), 591–595. <https://doi.org/10.1007/s10967-009-0210-8>.
- (99) Steeb, J.; Graczyk, D.; Tsai, Y.; Mertz, C.; Essling, A.; Sullivan, V.; Carney, K.; Finck, M.; Giglio, J.; Chamberlain, D. Application of Mass Spectrometric Isotope Dilution Methodology for ^{90}Sr Age-Dating with Measurements by Thermal-Ionization and Inductively Coupled- Plasma Mass Spectrometry. *J Anal Atom Spectrom* **2013**, *28* (9), 1493–1507. <https://doi.org/10.1039/C3JA50136A>.
- (100) Groska, J.; Vajda, N.; Molnár, Z.; Bokori, E.; Szeredy, P.; Zagyvai, M. Determination of Actinides in Radioactive Waste after Separation on a Single DGA Resin Column. *J Radioanal Nucl Ch* **2015**, *309* (3), 1145–1158. <https://doi.org/10.1007/s10967-016-4729-1>.

- (101) Murali, M.; Bhattacharayya, A.; Raut, D.; Kar, A.; Tomar, B.; Manchanda, V. Characterization of High Level Waste for Minor Actinides by Chemical Separation and Alpha Spectrometry. *J Radioanal Nucl Ch* **2012**, 294 (1), 149–153. <https://doi.org/10.1007/s10967-011-1571-3>.
- (102) Shimada, A.; Haraga, T.; Hoshi, A.; Kameo, Y.; Nakashima, M.; Takahashi, K. Analysis of Th, U, Pu, and Am in Radioactive Metal Waste Using Extraction Chromatography. *J Radioanal Nucl Ch* **2010**, 286 (3), 765–770. <https://doi.org/10.1007/s10967-010-0750-y>.
- (103) Yoon, S.; Ha, W. H.; Park, S.; Lee, S. S.; Jin, Y. W. Development and Optimization of an On-Site Sequential Extraction System for Radiobioassay in Radiation Emergency. *J. Radioanal. Nucl. Chem.* **2017**, 311 (2), 1053–1057. <https://doi.org/10.1007/s10967-016-4977-0>.
- (104) Brown, J. N. W. W.; Robertson, J. D.; Brockman, J. D. Measurement of U and Pu Isotope Ratios in Hair and Nail Samples Using Extraction Chromatography and Multi-Collector Inductively Coupled Plasma Mass Spectrometry. *Talanta* **2014**, 129, 481–485. <https://doi.org/10.1016/j.talanta.2014.06.015>.
- (105) Maxwell, S. L.; Culligan, B.; Hutchison, J. B.; Utsey, R. C.; Sudowe, R.; McAlister, D. R.; Daniel, M. Rapid Method to Determine Actinides and 89/90Sr in Limestone and Marble Samples. *J. Radioanal. Nucl. Chem.* **2016**, 310 (1), 377–388. <https://doi.org/10.1007/s10967-016-4783-8>.
- (106) Harrison, J.; Zawadzki, A.; Chisari, R.; Wong, H. Separation and Measurement of Thorium, Plutonium, Americium, Uranium and Strontium in Environmental Matrices. *J Env. Radioact.* **2011**, 102 (10), 896–900. <https://doi.org/10.1016/j.jenvrad.2010.05.010>.
- (107) Horowitz, E. P. Extraction Chromatography of Actinides and Selected Fission Products: Principles and Achievement of Selectivity.
- (108) Stratz, S.; Jones, S.; Oldham, C.; Mullen, A.; Jones, A.; Auxier, J.; Hall, H. Gas-Phase Detection of Solid-State Fission Product Complexes for Post-Detonation Nuclear Forensic Analysis. *J Radioanal Nucl Ch* **2016**, 310 (3), 1273–1276. <https://doi.org/10.1007/s10967-016-4920-4>.
- (109) Kučera, J.; Kameník, J.; Povinec, P. P. Radiochemical Separation of Mostly Short-Lived Neutron Activation Products. *J. Radioanal. Nucl. Chem.* **2017**, 311 (2), 1299–1307. <https://doi.org/10.1007/s10967-016-4930-2>.

- (110) Higginson, M.; Thompson, P.; Marsden, O.; Livens, F.; Harwood, L.; Lewis, F.; Hudson, M.; Heath, S. Rapid Selective Separation of Americium/Curium from Simulated Nuclear Forensic Matrices Using Triazine Ligands. *Radiochim Acta* **2015**, *103* (10), 687–694. <https://doi.org/10.1515/ract-2015-2403>.
- (111) Pestana, R.; Sarkis, J.; Marin, R.; Cassio, A.-J.; Carvalho, E. New Methodology for Uranium Analysis in Swipe Samples for Nuclear Safeguards Purposes. *J Radioanal Nucl Ch* **2013**, *298* (1), 621–625. <https://doi.org/10.1007/s10967-013-2467-1>.
- (112) Liezers, M.; Lehn, S. A.; Olsen, K. B.; Farmer, O. T.; Duckworth, D. C. Determination of Plutonium Isotope Ratios at Very Low Levels by ICP-MS Using on-Line Electrochemically Modulated Separations. *J. Radioanal. Nucl. Chem.* **2009**, *282* (1), 299–304. <https://doi.org/10.1007/s10967-009-0228-y>.
- (113) Badaut, V.; Wallenius, M.; Mayer, K. Anion Analysis in Uranium Ore Concentrates by Ion Chromatography. *J Radioanal Nucl Ch* **2009**, *280* (1), 57–61. <https://doi.org/10.1007/s10967-008-7404-3>.
- (114) Verma, S. P.; Santoyo, E. High-Performance Liquid and Ion Chromatography: Separation and Quantification Analytical Techniques for Rare Earth Elements. **2007**.
- (115) Byerly, B.; Stanley, F.; Spencer, K.; Colletti, L.; Garduno, K.; Kuhn, K.; Lujan, E.; Martinez, A.; Porterfield, D.; Rim, J.; et al. Forensic Investigation of Plutonium Metal: A Case Study of CRM 126. *J Radioanal Nucl Ch* **2016**, *310* (2), 623–632. <https://doi.org/10.1007/s10967-016-4919-x>.
- (116) Lee, M. H.; Ahn, H. J.; Park, J. H.; Park, Y. J.; Song, K. Rapid Sequential Determination of Pu, {⁹⁰Sr} and {²⁴¹Am} Nuclides in Environmental Samples Using an Anion Exchange and {Sr-Spec} Resins. *Appl Radiat Isot.* **2011**, *69* (2), 295–298. <https://doi.org/10.1016/j.apradiso.2010.09.018>.
- (117) Eikenberg, J.; Bajo, S.; Beer, H.; Hitz, J.; Ruethi, M.; Zumsteg, I.; Letessier, P. Fast Methods for Determination of Antropogenic Actinides and {U/Th-Series} Isotopes in Aqueous Samples. *Appl Radiat Isot.* **2004**, *61* (2–3), 101–106. <https://doi.org/10.1016/j.apradiso.2004.03.020>.
- (118) Eikenberg, J.; Jäggi, M.; Beer, H.; Rüthi, M.; Zumsteg, I. Separation Techniques for Low-Level Determination of Actinides in Soil Samples. *Appl. Radiat. Isot.* **2009**, *67* (5), 776–780. <https://doi.org/10.1016/j.apradiso.2009.01.034>.

- (119) Reboul, S.; Borai, E.; Fjeld, R. Sequential Separation of Actinides by Ion Chromatography Coupled with On-Line Scintillation Detection. *Anal Bioanal Chem* **2002**, *374* (6), 1096–1100. <https://doi.org/10.1007/s00216-002-1566-6>.
- (120) Borozdin, K. N.; Hogan, G. E.; Morris, C. L.; William, C.; Saunders, A.; Schultz, L. J.; Teasdale, M. E.; Cullen, J. L.; Clarkson, A.; Hamilton, D. J.; et al. No Title. *Ieee T Nucl Sci* **2008**, *51* (1), 2238–2244. <https://doi.org/10.1109/TNS.2004.836117>.
- (121) Xu, Y.; Qiao, J.; Hou, X.; Pan, S.; Roos, P. Determination of Plutonium Isotopes (^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu) in Environmental Samples Using Radiochemical Separation Combined with Radiometric and Mass Spectrometric Measurements. *Talanta* **2014**, *119*, 590–595. <https://doi.org/10.1016/j.talanta.2013.11.061>.
- (122) Smith, M. R.; Iii, O. T. F.; Reeves, J. H.; Koppelaar, D. W. Radionuclide Detection by Ion-Chromatography and Online ICPMS and Beta Detection: Fission Product Rare Earth Element Measurements. *J. Radioanal. Nucl. Chem.* **1995**, *194* (1), 7–13.
- (123) Fjeld, R.; T., D.; Leyba, J.; Paulenova, A. Measurement of Radionuclides Using Ion Chromatography and On-Line Radiation Detection. *J Radioanal Nucl Ch* **2005**, *263* (3), 635–640. <https://doi.org/10.1007/s10967-005-0636-6>.
- (124) Das, D.; Ansari, S.; Mohapatra, P.; Mary, G.; Radhakrishnan, K.; Tripathi, S.; Manchanda, V. Separation and Determination of Components of High Level Waste Using IC and Dynamically Modified Reversed-Phase HPLC in ‘Actinide Partitioning’ Studies Using Synthetic Waste Solution. *J Radioanal Nucl Ch* **2011**, *287* (1), 293–298. <https://doi.org/10.1007/s10967-010-0683-5>.
- (125) Miyamoto, Y.; Yasuda, K.; Magara, M. Sequential Separation of Ultra-Trace U, Th, Pb, and Lanthanides Using a Simple Automatic System. *Analyst* **2015**, *140* (13), 4482–4488. <https://doi.org/10.1039/C5AN00027K>.
- (126) Almon, A. C.; Kinard, W. F.; Dewberry, R. A.; Bibler, N. E.; Almon, J. A. C.; Kinard, W. F.; Dewberry, R. A.; Bibler, N. E.; Site, S. R. Multimodal Separation of Alkali, Alkaline Earth, Transition, Post-Transition, Lanthanide, and Actinide Metal Cations in Waste Sludge (U). In *Symposium for Ion Chromatography in the Power Industry*; New Orleans, LA, 1991.

- (127) Epov, V.; Lariviere, D.; Reiber, K.; Evans, R.; Cornett, R. Extraction and Determination of Cs in Natural Waters by ICP-MS after Ion Exchange Separation. *J Anal Atom Spectrom* **2004**, 19 (9), 1225–1229. <https://doi.org/10.1039/B403013C>.
- (128) Yang, G.; Tazoe, H.; Yamada, M. Rapid Determination of ^{135}Cs and Precise $^{135}\text{Cs}/^{137}\text{Cs}$ Atomic Ratio in Environmental Samples by Single-Column Chromatography Coupled to Triple-Quadrupole Inductively Coupled Plasma-Mass Spectrometry. *Anal Chim Acta* **2016**, 908, 177–184. <https://doi.org/10.1016/j.aca.2015.12.041>.
- (129) Liao, H.; Zheng, J.; Wu, F.; Yamada, M.; Tan, M.; Chen, J. Determination of Plutonium Isotopes in Freshwater Lake Sediments by Sector-Field ICP-MS after Separation Using Ion-Exchange Chromatography. *Appl Radiat Isot.* **2008**, 66 (8), 1138–1145. <https://doi.org/10.1016/j.apradiso.2008.01.001>.
- (130) Qiao, J.; Hou, X.; Roos, P.; Miró, M. Rapid Isolation of Plutonium in Environmental Solid Samples Using Sequential Injection Anion Exchange Chromatography Followed by Detection with Inductively Coupled Plasma Mass Spectrometry. *Anal. Chim. Acta* **2011**, 685 (2), 111–119. <https://doi.org/10.1016/j.aca.2010.10.029>.
- (131) Vassileva, E.; Han, E.; Levy, I. Determination of Low-Level Plutonium in Seawater by Sector Field Inductively Coupled Plasma Mass Spectrometry: Method Validation. *Environ. Sci. Pollut. Res.* **2017**, 24 (9), 7898–7910. <https://doi.org/10.1007/s11356-016-6633-1>.
- (132) Pointurier, F.; Hubert, A.; Roger, G. A Method for Dating Small Amounts of Uranium. *J Radioanal Nucl Ch* **2013**, 296 (2), 593–598. <https://doi.org/10.1007/s10967-012-2198-8>.
- (133) Byerly, B.; Kuhn, K.; Colletti, L.; Foster, L.; Keller, R.; Lujan, E.; Martinez, A.; Porterfield, D.; Schwartz, D.; Spencer, K.; et al. Chemical Investigation of Three Plutonium–Beryllium Neutron Sources. *J. Radioanal. Nucl. Chem.* **2017**, 312 (1), 95–104. <https://doi.org/10.1007/s10967-017-5192-3>.
- (134) Gautier, C.; Bourgeois, M.; Isnard, H.; Nonell, A.; Stadelmann, G.; Goutelard, F. Development of Cadmium/Silver/Palladium Separation by Ion Chromatography with Quadrupole Inductively Coupled Plasma Mass Spectrometry Detection for off-Line Cadmium Isotopic Measurements. *J Chromatogr A* **2011**, 1218 (31), 5241–5247. <https://doi.org/10.1016/j.chroma.2011.06.004>.

- (135) Solatie, D.; Carbol, P.; Betti, M.; Bocci, F.; Hiernaut, T.; Rondinella, V.; Cobos, J. Ion Chromatography Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS) and Radiometric Techniques for the Determination of Actinides in Aqueous Leachate Solutions from Uranium Oxide. *Fresenius' J Anal Chem* **2000**, 368 (1), 88–94. <https://doi.org/10.1007/s002160000536>.
- (136) Röllin, S.; Eklund, U. B.; Spahiu, K. Separation of Actinide Redox Species with Cation Exchange Chromatography and Its Application to the Analysis of Spent Fuel Leaching Solutions. *Radiochim. Acta* **2001**, 89, 757–763.
- (137) Röllin, S.; Eklund, U.; Rollin, S. Determination of U(IV) and U(VI) by Ion Chromatography– Inductively Coupled Plasma Mass Spectrometry and Its Application to Kinetic Studies. *J. Chromatogr. A* **2000**, 884, 131–141.
- (138) Barrero Moreno, J. M.; BETTI, M.; Garcia Alonso, J. I.; M. BARRERO MORENO, J.; BETTI, M.; I. GARCIA ALONSO, J. Determination of Neptunium and Plutonium in the Presence of High Concentrations of Uranium by Ion Chromatography–Inductively Coupled Plasma Mass Spectrometry. *J. Anal. At. Spectrom.* **1997**, 12 (3), 355–361. <https://doi.org/10.1039/A606359D>.
- (139) Röllin, S.; Kopatjtjic, Z.; Wernli, B.; Magyar, B. Determination of Lanthanides and Actinides in Uranium Materials by High-Performance Liquid Chromatography with Inductively Coupled Plasma Mass Spectrometry. **1996**, 739, 139–149.
- (140) Gourgiotis, A.; Isnard, H.; Nonell, A.; Aubert, M.; Stadelmann, G.; Dupont, E.; I., A.; Tiang, G.; Rao, L.; Lukens, W.; et al. Bk and Cf Chromatographic Separation and $^{249}\text{Bk}/^{248}\text{Cm}$ and $^{249}\text{Cf}/^{248}\text{Cm}$ Elemental Ratios Determination by Inductively Coupled Plasma Quadrupole Mass Spectrometry. *Talanta* **2013**, 106, 39–44. <https://doi.org/10.1016/j.talanta.2012.11.056>.
- (141) Betti, M. Environmental Monitoring of Radioisotopes by Mass Spectrometry and Radiochemical Methods in Urban Areas. *Microchem J* **2000**, 67 (1–3), 363–373. [https://doi.org/10.1016/S0026-265X\(00\)00090-4](https://doi.org/10.1016/S0026-265X(00)00090-4).
- (142) Bruzzoniti, M. C.; Cavalli, S.; Mangia, A.; Mucchino, C.; Sarzanini, C.; Tarasco, E. Ion Chromatography with Inductively Coupled Plasma Mass Spectrometry, a Powerful Analytical Tool for Complex Matrices Estimation of Pt and Pd in Environmental Samples. *J Chromatogr A* **2003**, 997 (1–2), 51–63. [https://doi.org/10.1016/S0021-9673\(03\)00547-8](https://doi.org/10.1016/S0021-9673(03)00547-8).

- (143) Bing, L.; Wei, L.; Hong-xia, Y.; Xiaoduan, L.; Deng-yun, C. Determination of Iodine Species Using {HPLC-ICP-MS}. **2006**, No. 29.
- (144) Wolf, S. F.; Bowers, D. L.; Cunnane, J. C. Analysis of High Burnup Spent Nuclear Fuel by ICP-MS. *J. Radioanal. Nucl. Chem.* **2005**, 263 (3), 581–586.
- (145) Winter, C.; Seubert, A. Usability of Online-Coupling Ion Exchange Chromatography ICP-AES/-MS for the Determination of Trivalent Metal Complex Species under Acidic Conditions. *J. Anal. At. Spectrom.* **2016**, 31 (6), 1262–1268. <https://doi.org/10.1039/c5ja00480b>.
- (146) Latkoczy, C.; Prohaska, T.; Watkins, M.; Maria, T.-N.; Stingeder, G. Strontium Isotope Ratio Determination in Soil and Bone Samples after On-Line Matrix Separation by Coupling Ion Chromatography {(HPIC)} to an Inductively Coupled Plasma Sector Field Mass Spectrometer {(ICP-SFMS)}. *J Anal Atom Spectrom* **2001**, 16 (8), 806–811. <https://doi.org/10.1039/B102797M>.
- (147) Hann, S.; Prohaska, T.; Köllensperger, G.; Latkoczy, C.; Stingeder, G. Separation of Spectral and Non-Spectral Interferences by on-Line High Performance Ion Chromatography Inductively Coupled Plasma Sector Field Mass Spectrometry (HPIC-ICP-SFMS) for Accurate Determination of ^{234}U , ^{235}U , ^{238}U and ^{232}Th in Industrial Ores. *J Anal Atom Spectrom* **2000**, 15 (6), 721–725. <https://doi.org/10.1039/B001076F>.
- (148) Truscott, J.; Jones, P.; Fairman, B.; Evans, E. Determination of Actinides in Environmental and Biological Samples Using High-Performance Chelation Ion Chromatography Coupled to Sector-Field Inductively Coupled Plasma Mass Spectrometry. *J Chromatogr A* **2001**, 928 (1), 91–98. [https://doi.org/10.1016/S0021-9673\(01\)01120-7](https://doi.org/10.1016/S0021-9673(01)01120-7).
- (149) Ežerinskis, Ž.; Spolaor, A.; Kirchgeorg, T.; Cozzi, G.; Vallenga, P.; Kjær, H.; Šapolaitė, J.; Barbante, C.; Druteikienė, R. Determination of ^{129}I in Arctic Snow by a Novel Analytical Approach Using IC-ICP-SFMS. *J Anal Atom Spectrom* **2014**, 29 (10), 1827–1834. <https://doi.org/10.1039/C4JA00179F>.
- (150) Karasinski, J.; Bulska, E.; Wojciechowski, M.; Krata, A. A.; Halicz, L. On-Line Separation of Strontium from a Matrix and Determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ Ratio by Ion Chromatography/Multicollector-ICPMS. *J. Anal. At. Spectrom.* **2016**, 31 (7), 1459–1463. <https://doi.org/10.1039/c6ja00109b>.

- (151) Silvia, G.-R.; Moldovan, M.; Alonso, J. Measurement of Strontium Isotope Ratios by MC-ICP-MS after on-Line Rb–Sr Ion Chromatography Separation. *J Anal Atom Spectrom* **2007**, *23* (1), 84–93. <https://doi.org/10.1039/B708936H>.
- (152) J., R.-C.; Silvia, G.-R.; Moldovan, M.; Alonso, J. Multiple Linear Regression and On-Line Ion Exchange Chromatography for Alternative Rb–Sr and Nd–Sm MC-ICP-MS Isotopic Measurements. *J Anal Atom Spectrom* **2012**, *27* (4), 611–618. <https://doi.org/10.1039/C2JA10274A>.
- (153) Guéguen, F.; Isnard, H.; Nonell, A.; Vio, L.; Vercoeur, T.; Chartier, F. Neodymium Isotope Ratio Measurements by LC-MC-ICPMS for Nuclear Applications: Investigation of Isotopic Fractionation and Mass Bias Correction. *J. Anal. At. Spectrom.* **2015**, *30* (2), 443–452. <https://doi.org/10.1039/c4ja00361f>.
- (154) Karasinski, J.; Bulska, E.; Wojciechowski, M.; Halicz, L.; Krata, A. High Precision Direct Analysis of Magnesium Isotope Ratio by Ion Chromatography/Multicollector-ICPMS Using Wet and Dry Plasma Conditions. *Talanta* **2017**, *165*, 64–68. <https://doi.org/10.1016/j.talanta.2016.12.033>.
- (155) Eppich, G.; Knight, K.; Timothy, J.-H.; Spriggs, G.; Hutcheon, I. Constraints on Fallout Melt Glass Formation from a Near-Surface Nuclear Test. *J Radioanal Nucl Ch* **2014**, *302* (1), 593–609. <https://doi.org/10.1007/s10967-014-3293-9>.
- (156) Michalski, R.; Jabłńska, M.; Szopa, S.; Łyko, A.; Jabłńska, M.; Szopa, S.; Łyko, A. Application of Ion Chromatography with ICP-MS or MS Detection to the Determination of Selected Halides and Metal/Metalloids Species. *Crit. Rev. Anal. Chem.* **2011**, *41* (2), 133–150. <https://doi.org/10.1080/10408347.2011.559438>.
- (157) Bourgeois, M.; Isnard, H.; Gourgietis, A.; Stadelmann, G.; Gautier, C.; Mialle, S.; Nonell, A.; Chartier, F. Sm Isotope Composition and Sm/Eu Ratio Determination in an Irradiated 15 Eu Sample by Ion Exchange Chromatography -Quadrupole Inductively Coupled Plasma Mass Spectrometry Combined with Double Spike Isotope Dilution Technique. *J Anal Atom Spectrom* **2011**, *26* (8), 1660–1666. <https://doi.org/10.1039/C1JA10070J>.
- (158) Inn, K.; Jerome, L.; Nour, S.; Brooks, G.; Steve, L.; Steiner, R.; Williams, R.; Patton, B.; Bostick, D.; Eiden, G.; et al. Ultra-Low Level Plutonium Isotopes in the NIST SRM 4355A (Peruvian Soil-1). *Appl Radiat Isot.* **2009**, *67* (5), 667–671. <https://doi.org/10.1016/j.apradiso.2009.01.007>.

- (159) Pointurier, F.; Williams, R.; Stephen, L.; Steiner, R.; Bostick, D.; Olsen, K.; Wogman, N. Round-Robins in the Area of Uranium and Plutonium Bulk Analysis of Environmental Samples. *J Radioanal Nucl Ch* **2013**, 296 (2), 599–608. <https://doi.org/10.1007/s10967-012-1985-6>.
- (160) Moreno, J.; Betti, M.; Nicolaou, G. Determination of Caesium and Its Isotopic Composition in Nuclear Samples Using Isotope Dilution-Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry. *J Anal Atom Spectrom* **1999**, 14 (5), 875–879. <https://doi.org/10.1039/a806467i>.
- (161) Perna, L.; Bocci, F.; Heras, L.; Pablo, J.; Betti, M. Studies on Simultaneous Separation and Determination of Lanthanides and Actinides by Ion Chromatography Inductively Coupled Plasma Mass Spectrometry Combined with Isotope Dilution Mass Spectrometry. *J Anal Atom Spectrom* **2002**, 17 (9), 1166–1171. <https://doi.org/10.1039/B202451A>.
- (162) Jian, Z.; Masatoshi, Y. Precise Determination of Pu Isotopes in a Seawater Reference Material Using ID-SF-ICP-MS Combined with Two-Stage Anion-Exchange Chromatography. *Anal Sci* **2007**, 23 (5), 611–615. <https://doi.org/10.2116/analsci.23.611>.
- (163) Erlandson, O. R. *Redox In-Line Monitoring Instruments Information Manual*; Richland, WA, 1959.
- (164) Eappen, K. P.; Sapra, B. K.; Mayya, Y. S. A Novel Methodology for Online Measurement of Thoron Using Lucas Scintillation Cell. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2007**, 572 (2), 922–925. <https://doi.org/10.1016/j.nima.2006.11.074>.
- (165) Orton, C. R.; Fraga, C. G.; Christensen, R. N.; Schwantes, J. M. Proof of Concept Simulations of the Multi-Isotope Process Monitor: An Online, Nondestructive, near-Real-Time Safeguards Monitor for Nuclear Fuel Reprocessing Facilities. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2011**, 629 (1), 209–219. <https://doi.org/10.1016/j.nima.2010.10.024>.
- (166) Yasuda, K.; Usuda, S.; Gunji, H. Development of Scintillation-Light-Transmission Type Phoswich Detector for Simultaneous Alpha- and Beta (Gamma)-Ray Counting. *IEEE Trans. Nucl. Sci.* **2000**, 47 (4 PART 1), 1337–1340. <https://doi.org/10.1109/23.872974>.

- (167) Vojtyla, P. Calibration of Monitors Used for Surveillance of Radioactivity in Effluent Water from CERN's Accelerator Installations. *Appl. Radiat. Isot.* **2001**, 55 (1), 81–88. [https://doi.org/10.1016/S0969-8043\(00\)00361-4](https://doi.org/10.1016/S0969-8043(00)00361-4).
- (168) Guoxiu, Q.; Xu, Y.; Wang, L.; Zhang, X.; Zhou, W.; Li, W. Design of an On-Line Monitoring System for Radioactive Wastewater. *J. Radioanal. Nucl. Chem.* **2017**, 314 (1), 215–220. <https://doi.org/10.1007/s10967-017-5356-1>.
- (169) Morley, S. M.; Seiner, B.; Finn, E.; Greenwood, L.; Smith, S. C.; Gregory, S.; Haney, M.; Lucas, D.; Douglas, M.; Metz, L. Integrated Separation Scheme for Measuring a Suite of Fission and Activation Products from a Fresh Mixed Fission and Activation Product Sample. *J. Radioanal. Nucl. Chem.* **2015**, 304, 509–515. <https://doi.org/10.1007/s10967-014-3826-2>.
- (170) Morrison, S. S.; Clark, S. B.; Eggemeyer, T. A.; Finn, E. C.; Hines, C. C.; King, M. D.; Metz, L. A.; Morley, S. M.; Snow, M. S.; Wall, D. E.; et al. Activation Product Analysis in a Mixed Sample Containing Both Fission and Neutron Activation Products. *J. Radioanal. Nucl. Chem.* **2017**, 314 (3), 2501–2506. <https://doi.org/10.1007/s10967-017-5563-9>.
- (171) Brooker, G.; Terasaki, W. L.; Price, M. G.; Brooker, G.; Terasaki, W. L.; Price, M. G. Gammaflow: A Completely Automated Radioimmunoassay System. *Science (80-.)*. **1976**, 194 (4262), 270–276.
- (172) Wilshire, F. W.; Lambert, J. P.; Butler, F. E. Rapid Radiochemical Separation of Selected Toxic Elements in Environmental Samples Prior to Gamma Ray Spectrometry. *Anal. Chem.* **1975**, 47 (14), 2399–2403. <https://doi.org/10.1021/ac60364a010>.
- (173) Comba, P.; Martin, B. *Molecular Modeling of Transition Metal and Rare Earth Coordination Compounds*, 1st ed.; Elsevier Inc., 2019; Vol. 73. <https://doi.org/10.1016/bs.adioch.2018.11.001>.
- (174) Rode, B. M.; Schwenk, C. F.; Hofer, T. S.; Randolph, B. R. Coordination and Ligand Exchange Dynamics of Solvated Metal Ions. *Coord. Chem. Rev.* **2005**, 249 (24), 2993–3006. <https://doi.org/10.1016/j.ccr.2005.03.032>.

- (175) Penchoff, D. A.; Peterson, C. C.; Camden, J. P.; Bradshaw, J. A.; Auxier, J. D.; Schweitzer, G. K.; Jenkins, D. M.; Harrison, R. J.; Hall, H. L. Structural Analysis of the Complexation of Uranyl, Neptunyl, Plutonyl, and Americyl with Cyclic Imide Dioximes. *ACS Omega* **2018**, 3 (10), 13984–13993. <https://doi.org/10.1021/acsomega.8b02068>.
- (176) Schulz, W. W. *Science and Technology of Tributyl Phosphate: Volume III Applications of TBP in Nuclear Fuel Processing*; Navratil, J., Burger, L., Bender, K., Eds.; CRC Press LLC, 1990.
- (177) Banerjee, S.; Mazumdar, S. Electrospray Ionization Mass Spectrometry: A Technique to Access the Information beyond the Molecular Weight of the Analyte. *Int. J. Anal. Chem.* 2012. <https://doi.org/10.1155/2012/282574>.
- (178) Dionex. *TN-23: Ion Chromatography of Lanthanide Metals*; 1991.
- (179) Linge, K. L.; Jarvis, K. E. Quadrupole ICP-MS: Introduction to Instrumentation, Measurement Techniques and Analytical Capabilities. *Geostand. Geoanalytical Res.* **2009**, 33 (4), 445–467. <https://doi.org/10.1111/j.1751-908X.2009.00039.x>.
- (180) Jarvis, K. .; Gray, A. L.; Houk, R. S. *Handbook of Inductively Coupled Plasma-Mass Spectrometry*; Viridian Publishing (United Kingdom), 2003.
- (181) Thermo Fisher Scientific. *ICAP-Q Operating Manual*; 2012.
- (182) Thermo Fisher Scientific. *ICAP Q Software Manual*; 2012.
- (183) Thermo Fisher Scientific. Chromeleon Chromatography Data System Software <https://www.thermofisher.com/order/catalog/product/CHROMELEON7#/CHROMELEON7>.
- (184) Ross, B. S.; Hieftje, G. M. Alteration of the Ion-Optic Lens Configuration to Eliminate Mass- Dependent Matrix-Interference Effects in Inductively Coupled Plasma-Mass Spectrometry. *Spectrochim. Acta* **1991**, 46B (9), 1263–1273.
- (185) Andren, H.; Rodushkin, I.; Stenberg, A.; Malinovsky, D.; Baxter, D. Sources of Mass Bias and Isotope Ratio Variation in Multi- Collector ICP-MS: Optimization of Instrumental Parameters Based on Experimental Observations. *J. Anal. At. Spectrom.* **2004**, 19, 1217–1224.

- (186) Fontaine, G. H.; Hattendorf, B.; Bourdon, B.; Detlef, G. Effects of Operating Conditions and Matrix on Mass Bias in MC-ICPMS. *J. Anal. At. Spectrom.* **2009**, *24*, 637–648. <https://doi.org/10.1039/b816948a>.
- (187) ThermoFisher. ICPMS Systems and Technologies <https://www.thermofisher.com/us/en/home/industrial/spectroscopy-elemental-isotope-analysis/spectroscopy-elemental-isotope-analysis-learning-center/trace-elemental-analysis-tea-information/inductively-coupled-plasma-mass-spectrometry-icp-ms-information/icp> (accessed Dec 3, 2018).
- (188) Yang, L.; Tong, S.; Zhou, L. A Critical Review on Isotopic Fractionation Correction Methods for Accurate Isotope Amount Ratio Measurements by MC-ICP-MS. *J. Anal. At. Spectrom.* **2018**, *33*, 1849–1861. <https://doi.org/10.1039/c8ja00210j>.
- (189) Begley, I. S.; SHarp, B. L. Characterisation and Correction of Instrumental Bias in Inductively Coupled Plasma Quadrupole Mass Spectrometry for Accurate Measurement of Lead Isotope Ratios. *J. Anal. At. Spectrom.* **1997**, *12*, 395–402.
- (190) Graczyk, D. G.; Mclain, D. R.; Tsai, Y.; Chamberlain, D. B.; Steeb, J. L. Correcting Nonlinearity and Mass-Bias in Measurements by ICP Quadrupole Mass Spectrometry. *Spectrochim. Acta Part B* **2019**, *153* (October 2018), 10–18. <https://doi.org/10.1016/j.sab.2019.01.003>.
- (191) Rodríguez-González, P.; Marchante-Gayón, J. M.; García Alonso, J. I.; Sanz-Medel, A. Isotope Dilution Analysis for Elemental Speciation: A Tutorial Review. *Spectrochim. Acta - Part B At. Spectrosc.* **2005**, *60* (2), 151–207. <https://doi.org/10.1016/j.sab.2005.01.005>.
- (192) Knoll, G. *Radiation Detection and Measurement*, 4th ed.; Wiley, 2010.
- (193) Challan, M. B. Gamma-Ray Efficiency of a HPGe Detector as a Function of Energy and Geometry. *Appl. Radiat. Isot.* **2013**, *82*, 166–169. <https://doi.org/10.1016/j.apradiso.2013.07.010>.
- (194) Schlesinger, T. E.; Toney, J. E.; Yoon, H.; Lee, E. Y.; Brunett, B. A.; Franks, L. Cadmium Zinc Telluride and Its Use as a Nuclear Radiation Detector Material. *Mater. Sci. Eng.* **2001**, *32*, 103–189.
- (195) Derbin, A.; Khusainov, A.; Muratova, V.; Mouratov, O.; Arlt, R. How to Process Best Gamma Spectra of CdTe and CdZnTe Detectors. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2001**, *458* (1–2), 169–174. [https://doi.org/10.1016/S0168-9002\(00\)01035-4](https://doi.org/10.1016/S0168-9002(00)01035-4).

- (196) Toney, J. E.; Schlesinger, T. E.; James, R. B. Modeling and Simulation of Uniformity Effects in CdZnTe Gamma-Ray Spectrometers. *IEEE Trans. Nucl. Sci.* **1998**, 45 (1), 105–113. <https://doi.org/10.1109/23.659560>.
- (197) ORNL. High Flux Isotope Reactor <https://neutrons.ornl.gov/hfir>.
- (198) Roach, B. D.; Fenske, E. K.; Ilgner, R. H.; Hexel, C. R.; Haverlock, T. J.; Giaquinto, J. M. Development of a Fast and Efficient Analytical Technique for the Isotopic Analysis of Fission and Actinide Elements in Environmental Matrices. *J. Chromatogr. A* **2018**, 1587, 155–165. <https://doi.org/10.1016/j.chroma.2018.12.029>.
- (199) Rearden, B. T. Oak Ridge National Laboratory SCALE Website <https://www.ornl.gov/scale/overview>.
- (200) Gauld, I. C.; Radulescu, G.; Ilas, G.; Murphy, B. D.; Williams, M. L.; Wiarda, D. Isotopic Depletion and Decay Methods and Analysis Capabilities in SCALE. *Nucl. Technol.* **2011**, 174 (2), 169–195. <https://doi.org/10.13182/NT11-3>.
- (201) Knowles, J. R. A Generalized Method for Fissile Mass Characterization Using Short-Lived Fission Product Gamma Measurements, University of Tennessee, Knoxville, 2016.
- (202) Ziegler, J. F.; Ziegler, M. D.; Biersack, J. P. SRIM - The Stopping and Range of Ions in Matter (2010). *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **2010**, 268 (11–12), 1818–1823. <https://doi.org/10.1016/j.nimb.2010.02.091>.
- (203) LibreText. Recrystallization [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Physical_Properties_of_Matter/Solutions_and_Mixtures/Case_Studies/RECRYSTALLIZATION](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/Solutions_and_Mixtures/Case_Studies/RECRYSTALLIZATION).
- (204) Hussain, S. T.; Khan, G. A.; Shabeer, M. Solubility of Oxalic Acid. *Asian J. Res. Chem.* **2012**, 5 (11), 1323–1330.
- (205) Bruner, W. M.; Sherwood Jr, L. T. Diglycolic Acid. *Ind. Eng. Chem.* **1949**, 41 (8), 1653–1656.
- (206) Bluhm. *A Systematic Study of the Purification of Oxalic Acid*; 1917.

- (207) *Passive Nondestructive Assay of Nuclear Materials*; Reilly, D., Ensslin, N., Smith Jr, H., Kreiner, S., Eds.; United States Nuclear Regulatory Commission, 1991.
- (208) Fenske, E. K.; Roach, B. D.; Glasgow, D. C.; Ilgner, R. H.; Giaquinto, J. M. Rapid Measurements of U235 Fission Product Isotope Ratios Using an Online, High-Pressure Ion Chromatography ICPMS Protocol with Comparison to Isotopic Depletion Models. *J. Radioanal. Nucl. Chem.* **2019**, 320 (1), 153–163. <https://doi.org/10.1007/s10967-019-06438-4>.
- (209) Roach, B. D.; Glasgow, D. C.; Fenske, E. K.; Ilgner, R. H.; Hexel, C. R.; Giaquinto, J. M.; Glasgow, D. C.; Fenske, E. K.; Ilgner, R. H.; Hexel, C. R.; et al. *ORNL TM-2017-697: Demonstration of a Rapid HPLC-ICPMS Direct Coupling Technique Using IDMS Project Report Part II*; 2017.
- (210) Gill, J. A. Rapid Dissolution for Destructive Assay of Nuclear Melt Glass, University of Tennessee, Knoxville, 2015.
- (211) Lide, D. *CRC Handbook of Chemistry and Physics*, 84th ed.; Lide, D. R., Ed.; CRC Press LLC: Boca Raton, FL, 2004.
- (212) Roach, B. D.; Fenske, E. K.; Glasgow, D. C.; Partridge, J. D.; Keever, T. J.; Giaquinto, J. M. Rapid Concentration and Isotopic Measurements of Ultra-Trace ²³⁵U Fission Products with Comparison to an ORIGEN Isotope Depletion Model. *Talanta* **2019**, 205 (June), 120079. <https://doi.org/10.1016/j.talanta.2019.06.079>.
- (213) BNL. National Nuclear Data Center <http://www.nndc.bnl.gov/>.
- (214) Fenske, E. K.; Roach, B. D.; Hexel, C. R.; Glasgow, D. C.; Stewart, I. R.; Partridge, J. D.; Giaquinto, J. M. Inline Gamma-Spectrometry of Fission Product Elements after Rapid High-Pressure Ion Chromatographic Separation. *J. Radioanal. Nucl. Chem.* **2020**. <https://doi.org/10.1007/s10967-020-07103-x>.
- (215) Gorry, P. A. General Least-Squares Smoothing and Differentiation by the Convolution (Savitzky-Golay) Method. *Anal. Chem.* **1990**, 62 (6), 570–573. <https://doi.org/10.1021/ac00205a007>.
- (216) LNHB. Laboratoire National Henri Becquerel <http://www.nucleide.org/>.

APPENDIX

Table 44. List of elements and the correlating standard used for each.

Element	Standard
Lithium	IV-ICPMS-71-D
Scandium	IV-ICPMS-71-D
Titanium	IV-ICPMS-71-B
Manganese	IV-ICPMS-71-A
Iron	IV-ICPMS-71-A
Cobalt	IV-ICPMS-71-A
Nickel	IV-ICPMS-71-A
Copper	IV-ICPMS-71-A
Zinc	IV-ICPMS-71-A
Gallium	IV-ICPMS-71-A
Germanium	IV-ICPMS-71-B
Arsenic	IV-ICPMS-71-A
Selenium	IV-ICPMS-71-A
Rubidium	IV-ICPMS-71-A
Strontium	IV-ICPMS-71-A
Yttrium	IV-ICPMS-71-D
Zirconium	IV-ICPMS-71-B
Niobium	IV-ICPMS-71-B
Ruthenium	IV-ICPMS-71-A
Rhodium	IV-ICPMS-71-C
Palladium	IV-ICPMS-71-C
Cadmium	IV-ICPMS-71-A
Tin	IV-ICPMS-71-B
Antimony	IV-ICPMS-71-B
Tellurium	IV-ICPMS-71-B
Cesium	IV-ICPMS-71-A
Barium	IV-ICPMS-71-A
Lanthanum	IV-ICPMS-71-A
Cerium	IV-ICPMS-71-A
Praseodymium	IV-ICPMS-71-A
Neodymium	IV-ICPMS-71-A
Samarium	IV-ICPMS-71-A
Europium	IV-ICPMS-71-A
Gadolinium	IV-ICPMS-71-A
Terbium	IV-ICPMS-71-D
Dysprosium	IV-ICPMS-71-A
Holmium	IV-ICPMS-71-A
Erbium	IV-ICPMS-71-A
Thulium	IV-ICPMS-71-A

Table 44 (cont.)

Element	Standard
Ytterbium	IV-ICPMS-71-A
Lutetium	IV-ICPMS-71-A
Tantalum	IV-ICPMS-71-B
Osmium	IV-ICPMS-71-C
Iridium	IV-ICPMS-71-C
Gold	IV-ICPMS-71-C
Thallium	IV-ICPMS-71-A
Lead	IV-ICPMS-71-A
Thorium	IV-ICPMS-71-A
Uranium	IV-ICPMS-71-A
	CRM U930-D
Neptunium	NIST SRM-4241a
Plutonium	IRMM-86
Americium	ORNL-WRM-Am
Curium	ORNL-WRM-Cm

MCNP Input File Example

Author: Fenske; CZT surrounded by source (in-line experiment)

```

c
c      Geometry Overview
c
c      _____
c      | | | | | | | |
c      | | | | | | | |
c      | Src | Al | |-CZT-| | Al | Src |
c      | | | | | | | |
c      |_____|_____|_____|_____|_____|_____|_____|
c
c RPP CZT 1x1x1cm3 crystal with 3.8cm OD 1mm thick Al housing
c Src is homogenized within light .5 g/cc 1mm cylinder outside Al housing
C
1 1 -6.0 -1 imp:p=1 $ CZT
2 0 1 -2 4 -5 imp:p=1 $ Open area
3 2 -2.7 2 -3 4 -5 imp:p=1 $ sides of Al housing
31 2 -2.7 -3 -4 41 imp:p=1 $ bottom of Al housing
32 2 -2.7 -3 5 -51 imp:p=1 $ top of Al housing
4 0 (61:-41:51) -99 imp:p=1
5 3 -0.5 3 -61 -51 41 imp:p=1 $ Liquid line (source location)

```

99 0 99 imp:p=0 \$ EoW
c END CELLS (next line must be blank)

C

=====
=====

C PART TWO: SURFACE CARDS

C

=====
=====

1 rpp -0.5 0.5 -0.5 0.5 -0.5 0.5 \$ CZT
2 cz 1.80 \$ inner Al housing
3 cz 1.90 \$ outer Al housing
4 pz -0.51 \$ Al housing - bottom of bottom
41 pz -0.61 \$ Al housing - top of bottom
5 pz 0.51 \$ Al housing - bottom of top
51 pz 0.61 \$ Al housing - top of top
61 cz 2.00 \$ Source outer

c

99 so 5

c

c END SURFACES (next line must be blank)

C

=====
=====

C PART THREE: DATA CARDS

C

=====
=====

mode p

c MATERIALS CARD

m1 48000 .9 30000 .1 52000 1 \$ CZT

c

m2 13000 1 \$ Al

c

m3 1000 .2 6000 0.8

c END OF MATERIALS CARD

c

c SOURCE CARD

sdef PAR=2 ERG=d1 X=d2 Y=d3 Z=d4 CEL=5

c Energy

si1 L 0.033568 0.035551 0.036027 0.04098 0.08012 0.133515

sp1 D 0.002 0.0246 0.045 0.00257 0.0136 0.1109

c X-axis geometry

si2 -2 2

```

sp2 0 1
c Y-axis geometry
si3 -2 2
sp3 0 1
c Z-axis geometry
si4 -0.61 0.62
sp4 0 1
c
c
c Tally
F8:p 1 $ photon pulse-height on cell 1
FT8 GEB 1.0499E-2 6.99E-3 1.7515E1
E8 0.0 0.01 999i 3.0 $ Energy bins
nps 1e7

```

ORIGEN Example Input File

```

=origen
solver{type=cram}
options{print_xs=yes}
'=====
=====
case(Irradiation){
  title="PT-1 Irradiation"
  lib{file="ft33f001"}
  time{
    t=[18l 1.0 1]                %time: one hour with interpolated time steps
    units="hours"
    start=0.0}
  flux=[20r 6.57e14]             %flux=[20r 6.5e14] for PT-1 irradiation of total flux 6.5e14
  mat{
    iso=[U235=81.089E-6, U238=5.019E-6, U234=8.91E-7]      %iso: 87ug of 93% HEU
    units=grams
  }
  print{
    fisrate=ABS
  }
  save{
    file="PT-1_Irradiation_HEU87.f71"
    steps=all
    time_units=seconds
  }
}
'=====
=====

```

```

case(Decay){
  title="PT-1 Decay"
  lib{file="ft33f001"}
  time{
    t=[18l 0.1 10]          %t=[18l 0.1 600] for 600 second decay
    units="seconds"
    start=0.0}
  flux=[20r 0]
  save{
    file="PT-1_Decay_HEU87.f71"
    steps=all
    time_units=seconds
  }
}
'=====
=====
case(Count){
  title="PT-1 Decay"
  lib{file="ft33f001"}
  time{
    t=[58i 12 24 48 144 178 193 514 1018]          %t=[18l 0.1 600] for 600 second
decay
  units="hours"
  start=0.0}
  flux=[60r 0 0 0 0 0 0 0]
  save{
    file="PT-1_Count_HEU87.f71"
    steps=all
    time_units=seconds
  }
}
'=====
=====
end

```

VITA

Emilie was born in Denver, CO and graduated from Mountain View High School in 2010. She received her undergraduate degree from the University of New Mexico in Nuclear Engineering December 2013. She then moved to Knoxville, TN to study nuclear security at the University of Tennessee, Knoxville under Dr. Howard Hall at the Institute for Nuclear Security. She received a master's degree in Nuclear Engineering December 2015, through research of radiation detection monitoring of broad areas using a UAV and a NaI detector. Once this was completed, she decided to continue with UTK for a PhD in Nuclear Engineering, studying chemical applications for nuclear forensics at ORNL.

Notably, over the course of both her undergraduate and graduate studies, Emilie interned at: Idaho National Laboratory, the Nuclear Regulatory Commission, Pacific Northwest National Laboratory, and Oak Ridge National Laboratory, in addition to attending the Radiation Detection for Nuclear Security Summer School at PNNL. Her work at ORNL began as an ORISE intern in the Nuclear Security Modeling group for ten months, then eventually became an ORAU post-master's research assistant in the Nuclear Chemistry and Isotopics Laboratory group.